71-903

McMILLAN, Robert Edward, 1921-
RELIABILITY ASPECTS OF SEMICONDUCTOR SURFACE
PROTECTIVE COATINGS.

Newark college of Engineering, D.Eng.Sc., 1970
Engineering, electrical

University Microfilms, A XEROX Company, Ann Arbor, Michigan

RELIABILITY ASPECTS OF SEMICONDUCTOR SURFACE PROTECTIVE COATINGS

By

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A DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

DOCTOR OF ENGINEERING SCIENCE IN ELECTRICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

Newark, New Jersey

1970

APPROVAL OF DISSERTATION

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FOR

DEPARTMENT OF ELECTRICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey

May, 1970

ABSTRACT

This research was directed towards the occurrence and importance of surface leakage in reverse biased semiconductor diodes and the relation of this leakage to the reliability of a device under use conditions. As a result of this study, it is possible to predict one important leakage mechanism after such back-biased diode units have been subjected to long periods of temperature and humidity. This theory is consistent with tests of commercially available units, some of which have very slight surface leakage and others very large surface leakage.

Further, the usefulness of various possible passivating coatings is critically analyzed on the basis of comparative physical constants and film formation techniques. The process of comparison of physical constants has led to further concepts that can result in fabrication techniques with an end product semiconductor with superior reliability characteristics.

A table of physical properties of Si, SiO, SiO_2, Si_3N_4 and Al_2O_3, more extensive than is available in a single published source, is contained in this dissertation.

In epoxy molded SCR's, used as diodes, the predominant leakage mode involves leakage along the oxide surface, and this mode of leakage does not occur until the epoxy resin has become

saturated with moisture. Silicon nitride, glass molded diodes have not exhibited this mode of leakage in tests exceeding 5000 hours.

Coatings of SiO_2 on silicon have been made by evaporation of silicon dioxide utilizing a CO_2 Laser in a vacuum chamber. High purity films can be deposited by this technique, both because of the rate of deposition and the lack of internal heaters or other complications.

These insulating layers, namely SiO, SiO_2, Si_3N_4 and Al_2O_3, can be removed by intense radiation of a wavelength of 10.5 microns. The use of this technique may eliminate chemical etch-operations, with the inherent possibility of surface retention of ions.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation and gratitude to the following:

Dr. Raj P. Misra who provided countless hours of relevant discussion and valuable criticism as the author's advisor throughout this endeavor.

Dr. Maurice Zambuto and Dr. Frederick Russell for guidance and as sources of inspiration.

Dr. Kenneth Sohn and Dr. Leonard Salzarulo for guidance and assistance in experimental work.

His wife, Ruth Regene, for her encouragement and patience.

The National Science Foundation for financial support for one year of research.

The many local industries, large and small, and government facilities whose technical assistance aided this work.

The many undergraduate students who directed their senior projects to supplement this research.

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CHAPTER I

INTRODUCTION

1. Purpose

This chapter relates the reliability of devices required in modern systems to the trends of device development and systems development. The principal interests are the physical events which adversely influence the ability of a given solid state component to maintain a surface leakage which is small compared to bulk leakage in a back biased semiconductor diode. To do this, it becomes germane first to discuss the changing nature of systems and systems reliability, then to discuss various aspects of physical reliability.

An important part of this chapter is the definition of surface. It will be shown in subsequent chapters that surface leakage consists of many components.

An introduction to the important physical laws governing surface leakage is covered in Chapter II of this dissertation.

Chapter III links the physical laws and methods of film formation of Chapter II with specific physical data of films to shed more light on the various leakage paths. Tests on commercial units are used in Chapter IV to verify the principal mechanism.

Chapter V makes further use of the physical data of ceramic films to evolve several new fabrication techniques that can further improve surface reliability.

2. History

Surface performance of semiconductors has assumed an increasingly important role in device reliability since the introduction of the transistor in the early 1950's. Although certainly some improvement was bound to occur as a by-product of normal progress of a new device, various trends forced the evolution of the diode and transistor to smaller and more reliable devices, and this inevitably focused attention on the surface. The percentage increase of silicon devices and the inherent lower leakage of a back-biased silicon junction added to the emphasis on the nature of the surface.

Actually the start of the trend towards equipment complexity occurred during World War II. Prior to this time, electronics was confined largely to unsophisticated communications equipment. The advent of large scale usage of such systems as radar, sonar, loran, electronic countermeasures equipment and increasingly complex radio equipment meant installations with hundreds rather than dozens of active devices [vacuum tubes at that time]. A typical fighting ship might have several thousand installed active devices, compared with a few hundred prior to this time. Inoperability of this equipment for large percentages of the time caused battle losses, and a beginning of concern for device reliability.

3. Influence of Device Reliability on System Reliability

If a constant number of failures per unit of time is assumed for each component, it can be shown[1] that the Poisson distribution:

$$\frac{\sum e^{-a} a^{n}}{n!}$$

where: e is the Napierian Base 2.71 + . . .

n is an integer, including 0, 1, 2 . . .

a is a constant, in the case subsequently used, $a = rt$ where r is the expected number of failures in a unit of time, and t is the time

will give the probability of exactly 0, 1, 2, 3 . . . K failures by considering, respectively, the 1st Poisson (n = 0), 2nd (n = 1), 3rd (n = 2) . . . Poisson terms.

Using only the first term of Poisson's distribution, the probability of survival or reliability of the component is:

$$P_s = e^{-rt} \qquad \text{(eq. 1)}$$

where $r = \frac{\text{expected no. of failures experimentally determined}}{\text{unit of time}} = \frac{1}{m}$

---

[1] Calabro, S.R., Reliability Principles and Practices. New York: McGraw-Hill Book Co., 1962, pp 57-75.

t = time in operation since last repair

m = mean time between failures

If each component is vital, barring redundancy, one component failure will mean failure of the system. If a piece of equipment has n components, the probability of survival of all of these components for a time T is:

$$P_{equip} = P_{s1}\, P_{s2}\, P_{s3}\, P_{s4}\, P_{25} \;.\;.\;.\;.\;.\; P_{sn} \qquad \text{(eq. 2)}$$

From equation 1 and 2, we have:

$$P_{equip} = e^{-r_1 t}\, e^{-r_2 t}\, e^{-r_3 t} \;.\;.\;.\;.\;.\; e^{-r_n t}$$

$$= e^{-(r_1 + r_2 + r_3 + \;.\;.\;.\;.\;.\;.\; + r_n)t} \qquad \text{(eq. 3)}$$

A numerical example may help to show the effect of equipment complexity:

> If like components are assumed with a mean time between failure of 1000 hrs., or a failure rate of 0.001 units per hour, it is now possible to compare the probability of survival over 10 hours of each of two pieces of equipment, one with an installation of 100 components, the other with 1000. Equation 3 may be used if failure of any one or more components means failure of the equipment.

$$P_{\text{equip } 100} = e^{-(.001)(100)10} = 37\%$$

$$P_{\text{equip } 1000} = e^{-(.001)(1000)10} = \frac{1}{e^{10}} \approx .01\%$$

This comparison illustrates the meat of the problem by the use of hypothetical rates that are much higher than actual failure rates to be expected with modern semiconductors, by hypothesizing a much lower complexity factor than current or proposed systems. The trend from 1950 to present has led to tens of thousands of components instead of thousands. Certainly 100,000 components is no longer out of the ordinary. It has been stated that an Apollo rocket has over 2,500,000 functioning parts.

Beyond the moderately complicated radars and sonars the years have produced ultra complex computerized rocket systems with an array of complex detectors on board, and elaborate communications links to the ground environment. The ground environment can include automatic rocket check out, take off control and communications linked tracking stations. Engineering considerations dictate very stringent requirements on the components, including semiconductors, which can be tolerated in such an environment.

4. Small Size; Low Power; High Speed

Any equipment, whether airborne or rocket installed requires an increased fuel cost for each increased pound of payload. Hence, a second requirement is now added to the necessity for very low failure rates. Each component must be as light as possible. Hand in hand with low mass is small size, since a large package would in turn require a larger airframe or rocket frame and in turn more weight.

If redundant circuitry is used to increase the reliability a still further incentive to decrease size and weight is present.

Active device characteristics are indirectly controlled from another consideration of size and weight. Transistors and diodes consume power, and if the purpose of the device is to process information (i.e. this represents small, signal equipment), the power is largely wasted. Such small signal equipment is herein shown to place a more stringent leakage requirement on the semiconductor. The attendant large power supplies add weight and size to the electronics package. Furthermore, expended power produces heat which must be dissipated. This latter consideration is one of great importance for devices utilized in a fixed location as well as those destined for air or space travel.

Small power consumption implies low voltage and/or low current. If the operating current is low, reverse currents must also be low to prevent ambiguity of data. Other current leakages [such as surface leakage] must likewise be minimized.

In general, with the increased size of a device, an increase in surface leakage will occur and in some instances this leakage will be of importance simply as a quantity of current. More important, usually, is the relative contribution of the surface leakage to the combined leakage of surface and bulk across a back-biased junction. Under such a consideration, what is the effect of increasing the size of a device? That important part of the surface is the curve of intersection of the surface with a "p" - "n" junction which is back biased.

If the linear dimensions of a device are doubled and no change is made on the shape factor, the length of the curve of intersection of junction and surface is doubled. Under conditions of identical surface protection and contamination factors, a given back bias voltage should double the surface leakage. Under the condition of doubling of dimensions, however, the area of the junction between "p" and "n" should increase by a factor of 4. Since I_o (the reverse saturation current) is a linear function of the area[2], the bulk leakage should rise by a factor of four.

In a very large device, the inherent bulk leakage, I_o, will be high. This will not usually interfere with the proper operation of the device, since we would expect the possibility of very large forward currents and few circuit designs that

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[2] Lindmayer, Joseph and Charles Y. Wrigley, Fundamentals of Semiconductor Devices. Princeton, New Jersey: D. Van Nostrand Company, Inc., 1966, pp 29.

would call for a current approaching zero in the reverse direction. It is under these suppositions that the following statement is made. The contribution of the leakage current due to surface leakage will have less importance in large devices than in nearly identical small devices.

1950-1960 devices were protected in cans or glass envelopes. Clearly,this can or glass blob adds mass and bulk. Interconnections between devices add more mass. Protection without the can and multiple units become very desirable additions to the improvements needed, and the concept of integrated circuit has become a firm reality along with the added stringency of surface protection for the semiconductor devices.

Manufacturing cost of the devices, mentioned earlier, also directs effort in the direction of diffused planar devices with very little bulk depth, and a relatively large surface to be protected.

Shock and vibration requirements have enhanced reliability with fewer soldered connections. The evaporated aluminum wiring runs on an integrated circuit have their own reliability problems, including those of the insulating thin films!

Modern computers require computing speeds in microseconds and devices that act in nanoseconds. Again, low current and very small devices are resulting requirements. The low current must be accompanied by low leakage, moreover, some caution must be exercised that the films not be considered as simply "non-conductors." A considerable body of knowledge is being developed regarding electronic behavior of dielectric films. Included are such events as migration of ions, electrode injection mechanisms, polarization and trapping levels.

These non ohmic behaviors will not invariably be important, but are important with one class of device, the insulated gate field effect transistor (IGFET). This dissertation will not be primarily concerned with all of these behaviors, but some of them will be utilized in the following chapters. In any case, the interest will be primarily in the physical manifestations.

5. Reliability Factors

It has been stated[3] that Reliability, R, of semiconductor devices [and in fact of electronic devices in general] is a function of:

$$R \longrightarrow f \qquad \left\{ \begin{array}{l} \text{E - Electric Field} \\ \text{S - Surface} \\ \text{P - Package} \\ \text{A - Ambient Gases} \\ \text{T - Temperature and Temperature Gradient} \\ \text{S - Special Effects} \end{array} \right.$$

---

[3] Misra, Raj P., Proceedings of the Fifth Annual Conference on Basic Failure Mechanisms and Reliability in Electronics, Institute of Electrical and Electronic Engineers, Newark, New Jersey, June 15, 1964.

All of these factors are important in extending the life of a semiconductor device. In Chapter III these factors are related (along with the physical properties of the insulating layers) to predict expected failure modes in the surfaces of semiconductors.

From a reliability standpoint, various facets of device performance attributable to surface activity are apparent. Five of these are listed to define the problem, but this dissertation will deal specifically with only three of these areas. Failure rate determination and non-destructive advance prediction are only touched upon in this dissertation.

6. Bulk and Surface Effects

First of all, it is required to distinguish between the fall off of performance which is due to the surface, from that deterioration which has been caused by bulk properties or other portions of the package that may contribute. Since in a diode or bipolar device this can only be manifested by increased current, we must distinguish the increase in current (surface and bulk) from that due to the package lead-through terminals (if such exist) if the wire connections to the "n" or "p" layers touch any surface.

In a field effect device the same type of layers used for protection of diodes and diffused transistors are utilized between the gate and the body of the field effect transistors.

It is conceivable that in such a case contamination could cause an apparent open circuit between source and drain for normal signal voltages. Since these layers are so closely related physically to surface protective layers, there will be no attempt to discriminate between the two types, although the testing program almost exclusively utilizes diodes.

It may be necessary to make supplementary measurements on a unit that has failed beyond specified readings. The resulting values as some parameter is changed may be characteristic of surface leakage. On the other hand, the nature of the testing experiments can often help to distinguish between surface failure and bulk failure. For example, if readings are out of specification on a series of units tested at a given temperature with high humidity, but not out of specifications on similar units tested at the same temperature at low humidity, considerable justification exists for attributing this failure to surface. Even if there were some reason to believe that the bulk were affected by the humidity, the surface is still suspect by virtue of its low diffusion permeability, and the very low permeability of the crystalline silicon.

7. Determining Failure Rate

The second area of reliability interest is the determination of the rate of failure due to surface effects. As has been portrayed earlier in this chapter, the failure rates for a system with 100,000 components must be fantastically small. If it is postulated, for example, that a failure rate of 0.01% per thousand hours were attributable to surface, then 10,000,000 component hours of testing will be required, on the average to produce one failure. A higher magnitude of component hours than this value will be required to determine a rate of failure. This is a crucial point in the reliability consideration of any component. If the failure rate is even moderately close to that required for a modern complex system, the expense of testing to determine the failure rate is excessive. Each design or process change may require a re-test program as expensive as the one which originally determined that the device was not satisfactory. Even in the case that the unit is successful in its first series of tests, the problem of drift of any manufacturing procedure or process or incoming raw materials makes it highly desirable to possess a shorter term method of determining rates.

It is known that any physical system stressed beyond its normal operating parameters will exhibit a higher failure rate. Temperature is a favorite accelerating stress factor since it causes somewhat predictable changes in rates of failure involving chemical change or diffusion. This will be discussed more fully in Chapter II. If a rate can be accelerated by a factor of 10 to 20 the testing program to determine failure rates is greatly reduced in cost.

If this method is utilized, caution must be observed lest a second or third failure mechanism which is insignificant at normal operating temperature becomes dominant at the higher temperature. Further, the user of this technique also risks the possibility that the usual failure mode disappears at high temperature due to a change in state of some part of the device. Lewis and Bohrer[4] cite specific examples of both of these possibilities in the case of resistor failures.

8. Physical Reliability

The third reliability consideration involves the physical aspects of the device itself. If every electrical, mechanical, chemical, thermal or other stress can be exactly defined, device statistics can be predicted accurately, providing one has an equally exact knowledge of the characteristics of the films and their interaction with the underlying silicon. As would be expected, such precise knowledge of behavior does not exist at this time. Chapter II is concerned with the most common physical effects of dielectric film behavior, as well as with an exposition of current methods of film formation.

Chapter III contains a tabular listing of physical properties of the usual films, in comparison with the substrate material, silicon.

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[4] Lewis, C.W., J.J. Bohrer. "Physics of Resistor Failure", pp 11-19 of M. F. Goldberg and J. Vaccaro, Physics of Failure in Electronics. Baltimore: Spartan Books, 1963.

This table of physical constants and the methods of failure predicted thereby may be of use in future engineering designs which involve these same or similar materials in a similar manner. This is a fourth area of interest in which either the basic design or the techniques for forming the device and protective films are open for any new thoughts that will eliminate stress or better enable the assembly to stand stress. Chapter V explores a new direction in this regard specifically directed toward silicon dioxide (SiO_2) or aluminum oxide (Al_2O_3), but with possibilities beyond this.

9. Non-Destructive Advance Prediction

A fifth area of importance in these devices as well as any electronic devices with very low failure rates concerns the capability of making nondestructive measurements of any kind at any time during manufacturing or test by which future failures could be detected. Dr. Young D. Kim[5] approached this for diodes utilizing noise measurements. His measurements of single frequency noise *vs.* current provided some basis of hope for this technique to be useful in the future. Whether noise would be useful in these surface predictions is not known. No experiments along these lines were conducted in the present

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[5] Kim, Young Duck, *Noise Spectral Density as a Diagnostic Tool for Reliability*, Doctoral Dissertation, Newark College of Engineering, Newark, New Jersey, 1968.

study[6]. In Chapter III, section 11, the possibility of ionization in porous material is discussed. Kim's technique might be useful for layer development measurements as well as device reliability prediction.

10. Definition of Surface

The term "surface" in a consideration of surface protective layers bears careful definition. It is the interpretation of this writer that surface shall include any extension of the bulk that affects the overall electrical properties of the semiconductor, namely silicon. In the case of a deep underlying substrate of silicon there is only one "surface" exposed. The depth of the silicon is usually about .010" or 0.25 mm. The interface of any back-biased diodes or collector base junctions breaks the surface of the silicon on only one side of the silicon. It is at such an interface surface that actions other than bulk mechanisms take place.

Future devices may take advantage of the ability to coat very thin epitaxial layers of silicon on an insulating substrate. This opens the possibility that a layer may break through the bottom of the silicon, providing an interface for which the substrate will serve as a surface. In this event some or all of the ways in which insulative layers on top of the silicon

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[6] McWhorter, A.L., "1/f Noise and Germanium Surface Properties," Semiconductor Surface Physics, [Edited by R. H. Kingston], Philadelphia: University of Pennsylvania Press, 1957.

can affect device performance will manifest themselves in the bottom surface.

While this break-through to the bottom surface (at this moment) represents pure speculation, it is still the concern of the reliability engineer. If, indeed, future device malfunction may be suspected due to design trends in the direction of the utilization of thinner and thinner silicon layers, then it is the responsibility of the reliability engineer to warn the design engineer of possible future difficulty if an additional surface is added to the device; especially since this new surface may differ considerably from the top or open surface.

The top surface is more complex than might appear at first. Silicon dioxide, silicon nitride or similar coatings, whether grown or deposited, are usually confined to about 1 micron (10,000 Å) and often may be only a few thousand angstrom units in thickness. The disadvantages of heavier coatings are many. If the coating is grown, such as silicon dioxide, the mechanism of growth is diffusion limited, which means continually slower growth as the thickness increases. Some films tend to crack with large thickness. If the film is to serve as a diffusion mask, and is itself *etched*, undercutting will be much more serious in greater thicknesses. Excessive total strength of the oxide layer may mean very large tension in the silicon surface interface, which could provice a larger number of dislocations than usual.

Beyond a thin oxide or nitride surface, some other further protection is required to prevent contamination of the top of the first protective layer. To demonstrate this, observe first that the resistivity of some surface protecting materials may be in the neighborhood of 10^{12} ohm-cm. If it is postulated that a relatively low leakage resistance exists on top of the insulating layer, we might anticipate a voltage drop through the layer from a few volts to several hundred volts, depending on the extent and nature of the surface contamination.

If we assume a uniform voltage drop of 100 volts through the layer and an area of 0.01 sq. cm. above one active element, the leakage would be:

$$i = \frac{V}{R} = \frac{100}{\frac{10^{12} \times 5000 \times 10^{-8}}{0.01}} = \frac{1}{5 \times 10^{7}} = 20 \text{ nano amps}$$

Twenty nano amperes, under the circumstance of a very low leakage requirement might be excessive. Yet the 100 volts across the 5000 Å would not exceed the field strength of the layer.

$$E = \frac{100}{5000 \times 10^{-8}} = 2 \times 10^{6} \text{ volts/cm.}$$

It might be noted, however, that a field of $E = 2.0 \times 10^{6}$

volts/cm. is sufficiently high to cause ion migration, polarization or other instabilities. Hence, in grown or deposited Si_3N_4, $Si0_2$, Si0 or Al_20_3 a single layer will not suffice, and an overcoating will be necessary to prevent contamination of the surface which could cause leakage. Thus from a practical point of view, all layers that may contribute to the device performance must be included.

11. Secondary Coatings

In Chapter IV of this dissertation, commercial units with various encapsulants to protect the primary passivation are tested under an accelerating environment.

Aside from leakage of the top surface, contamination may supply ions which will migrate to the insulator silicon interface. Water vapor may prove damaging or may supply an ionizable media which may encourage other reactions to take place. In this same light, it might be extremely wise to supply whatever second coating is used with a deficiency of monovalent positive ions, absorbed water or other possibly harmful agents.

Possible materials for second coatings include glasses, epoxy resin, silicone rubber as well as silicone resin, and probably many other organic and inorganic compounds. The

Russians had in 1964 published material on the effectiveness of low melting point sulphur based "glass" as a primary coating.[7] This and other low melting point glasses cannot be excluded as a secondary coating. Gamen, Sirotkin and Stenina used 24% arsenic, 67% sulphur, and 9% iodine.

The specific tests of encapsulated units in Chapter IV reveal that glass was an exceptionally good secondary encapsulant, whereas epoxy resin was not. This statement will be further amplified and qualified in Chapter IV.

12. Synopsis

Modern space age systems require smaller, more reliable devices. Surface leakage is an important consideration in small signal integrated circuit devices. The surface itself is complex, and the possible paths of leakage are many. Secondary coatings are necessary where any possibility of contamination exists.

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[7] Gaman, V.I., A.A. Sirotkin, and V.M. Stenina. "Effect of Low Melting Glasses of the As-S-I System on the Current-Voltage Characteristics of Silicon p-n Functions", Surface Properties of Semiconductors, Edited by Fromkin, A.N., New York: Consultants Bureau, 1964, pp 147-150.

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[3] Misra, Raj P., Proceedings of the Fifth Annual Conference on Basic Failure Mechanisms and Reliability in Electronics, Institute of Electrical and Electronic Engineers, Newark, New Jersey, June 15, 1964.

[4] Lewis, C.W., J. J. Bohrer, "Physics of Resistor Failure," pp 11-19 of M. F. Goldberg and J. Vaccaro, Physics of Failure in Electronics. Baltimore: Spartan Books, 1963.

[5] Kim, Young Duck, Noise Spectral Density as a Diagnostic Tool for Reliability, Doctoral Dissertation, Newark College of Engineering, Newark, New Jersey, 1968.

[6] McWhorter, A.L., "1/f Noise and Germanium Surface Properties," Semiconductor Surface Physics, [Edited by R. H. Kingston], Philadelphia: University of Pennsylvania Press, 1957.

[7] Gaman, V.I., A.A. Sirotkin, and V.M. Stenina, "Effect of Low Melting Glasses of the As-S-I System on the Current-Voltage Characteristics of Silicon p-n Functions," Surface Properties of Semiconductors, Edited by Fromkin, A.N., New York: Consultants Bureau, 1964, pp 147-150.

CHAPTER II

THEORETICAL CONSIDERATIONS AND SUMMARY OF DEPOSITION METHODS

1. Foreword

Although much of the background material required is presented in Chapters III, IV, and V, certain additional background is essential to understand the roll played by semiconductor surfaces. In this chapter a brief outline is presented of the mechanisms which have a relevance to the change in conductivity of semiconductor surfaces. In addition a section on the structural roles of Pauling and Zachariasen are included with comment on the potential applicability of this information to the comparative behavior of films of silicon dioxide and silicon nitride.

2. Band Structure

With the advent of ultra high purity, nearly perfect, crystalline structures and quantum mechanics, theoretical workers have generated a model that seems to closely approximate the actual behavior of the semiconductor.

This development assumes the existence and validity of Schroedinger's equation, and starts with the usual consideration of electrons in a crystalline structure, which may be approximated by a series of potential wells. It suffices for the illustrative purposes of this development to consider single dimensional wells with vertical walls, extending infinitely in the + and - x directions. See Figure II-1 (a).

The following development, utilizing a solution attributed to Bloch, is included without reference. Almost any standard text dealing with solid state physics contains a similar treatment of Schroedinger's equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2}(E - V)\psi = 0 \qquad \text{eq. 1}$$

where ψ is the wave function

m is the mass of the electron $m = 9.11 \times 10^{-31}$ kgm

V is the potential energy as a function of

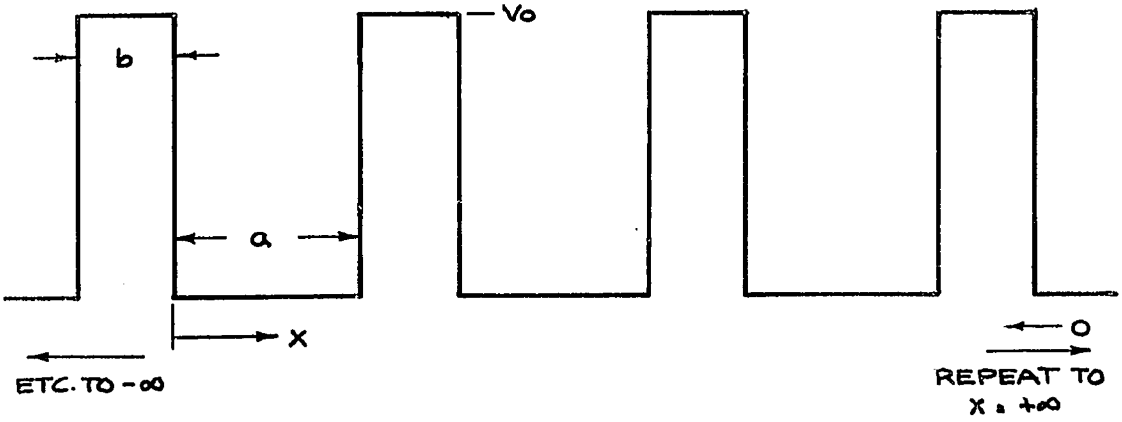
E is the Schroedinger separation constant for time and distance, identified with the energy of the electron.

$\hbar$ is $\frac{h}{2\pi}$ where h is Planck's constant; $h = 6.63 \times 10^{-34}$ j sec.

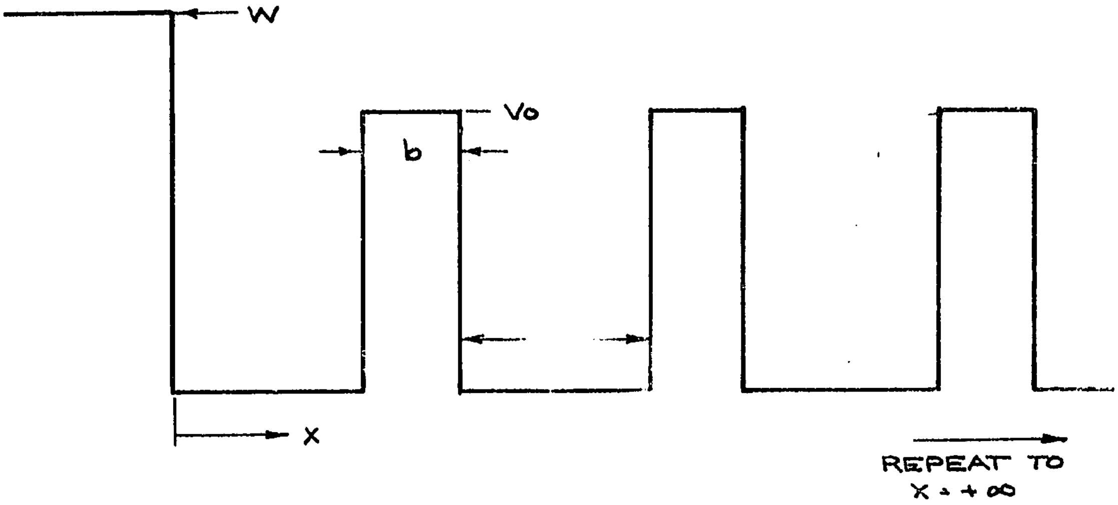
Two equations result since the potential has two constant values, Vo and 0.

$$\frac{d^2\psi_1}{dx^2} + \frac{2m}{\hbar^2} E\psi_1 = 0 \quad \text{for } 0 \leq x \leq a \qquad \text{eq. 1(a)}$$

$$\frac{d^2\psi_2}{dx^2} + \frac{2m}{\hbar^2}(E - V_o)\psi_2 = 0 \quad \text{for } -b \leq x \leq 0 \text{ or } a < x < a+b \qquad \text{eq. 1(b)}$$



(a) NON-TERMINATION



(b) TERMINATION AT ONE END

FIG. II - 1 SEMICONDUCTOR SINGLE DIMENSIONAL POTENTIAL WELL REPRESENTATION (a) NON-TERMINATION, (b) TERMINATION AT ONE END.

A solution is assumed (according to Bloch)

$$\psi = e^{\pm ikx} U_k (x)$$

$$\text{where } U_k (x) = U_k (x + (a + b))$$

$$\alpha^2 = \frac{2m}{\hbar^2} E \quad \text{and}$$

$$\beta^2 = \frac{2m}{\hbar^2} (V_o - E)$$

Substitute α and β into 1a and 1b, the result is

$$\frac{d^2U_1}{dx^2} + 2ik \frac{dU_1}{dx} + (\alpha^2 - k^2) U_1 = 0 \qquad \text{eq. 2(a)}$$

$$\frac{d^2U_2}{dx^2} + 2ik \frac{dU_2}{dx} - (\beta^2 - k^2) U_2 = 0 \qquad \text{eq. 2(b)}$$

whose solutions are:

$$U_1 = Ae^{i(\alpha - k)x} + Be^{-i(\alpha + k)x} \qquad \text{eq. 3(a)}$$

$$\text{and} \quad U_2 = Ce^{(\beta - ik)x} + De^{-(\beta + ik)x} \qquad \text{eq. 3(b)}$$

And whose boundary conditions are:

$$U_1(o) = U_2(o); \; U_1(a) = U_2(-b)$$

and $$\left.\frac{dU_1}{dx}\right|_{x = o} = \left.\frac{dU_2}{dx}\right|_{x = o}$$

$$\left.\frac{dU_1}{dx}\right|_{x = a} = \left.\frac{dU_2}{dx}\right|_{x = -b}$$

Four sets of equations in A, B, C & D result. By way of illustration, the first is

$$A + B = C + D$$

when these equations are combined, the following result occurs:

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh\beta b \sin\alpha a + \cosh\beta b \cos\alpha a = \cos k(a + b) \qquad \text{eq. 4}$$

This is often further simplified by letting the potential, V, approach infinity and distance, b, approach zero, but a great deal can be done with the expression as it stands.

Since for real k the right-hand side of this equation is always between ± 1, any combination of β and α for a given a & b spacing which results in a solution greater than +1 or less than -1 cannot satisfy the conditions imposed. Values of imaginary k or complex k are not permitted in the model chosen, since then:

$\psi = e^{(\text{real})\,x}\,U_k x$ and this would become boundless as x approaches plus or minus infinity depending on the sign of the original k.

Since α is a function of E and β is a function of E and Vo, with Vo fixed by a given physical situation, the left-hand side of equation 4 is a function of E and some values of E are permitted while others are not.

This concept, similar in many respects to the Bohr quantized energy levels for a single hydrogen like atom, is useful in explaining the difference in insulators, semiconductors and metallic conductors. Although that is not the purpose of this development, an abbreviated treatment is included to at least show the approach used in almost every semiconductor text.

For a single particle in a three-dimensional, very deep potential well, it can be shown that the boundary conditions are satisfied for integral values of n_x, n_y and n_z if energy levels are permitted:

$$E = \frac{h^2 \pi^2}{2m\ L^2}\ (n_x^2 + n_y^2 + n_z^2)$$

By a consideration of the number of energy levels in an element of volume of phase space for a constant value of $(n_x^2 + n_y^2 + n_z^2)$ it can further be shown that

$$g(E) = C\sqrt{E}$$

where g(E) is the energy density and C is a constant.

However, there is not an equal probability that each of the energy levels shall be occupied. By considering that there may be many ways to distribute N particles on G states, and that the higher the number of possibilities, the higher the system is disordered. A quantity called entropy is defined as the natural logarithm of the disorder, or the log of the number of equally probable configurations of any system.

Considering a system of electrons in a semiconductor, two additional constraints are added: (1) there are a smaller number of available electrons than the number of available states, and (2) only one electron is allowed in each state. An electron with a spin of + 1/2 is considered to be in a different state than one with a spin of - 1/2. This latter is called the Pauli Exclusion Principle. The statistics generated are termed Fermi-Dirac.

The number of equally probable distributions turns out to be:

$$W_s = \frac{G_s!}{N_s!(G_s - N_s)!} \qquad \text{eq. 5}$$

where: N_s = number of electrons in state s

G_s = number of available s states

Since the total number of electrons is equal to the sum of electrons in the various energy states, $N = \sum_s N_s$. Further, the total energy is described by $E = \sum_s E_s N_s$. The expression:

$\alpha(N - \Sigma_s N_s) + \beta(E - \Sigma_s E_s N_s)$ is added to $\ln W_s$ and the entropy is maximized. It follows that:

$$N_i = \frac{G_i}{1+e^{\alpha+\beta E_i}}$$

The arbitrary constant β is evaluated by thermodynamic considerations, and α by physical reasoning.

$$N_i = \frac{G_i}{1+e^{\frac{E_i - E_f}{kT}}} \qquad \text{eq. 6}$$

where E_f = Fermi Level

k = Boltzman's constant

T = Temperature in degrees Kelvin

N_i = Number electrons in the ith energy state

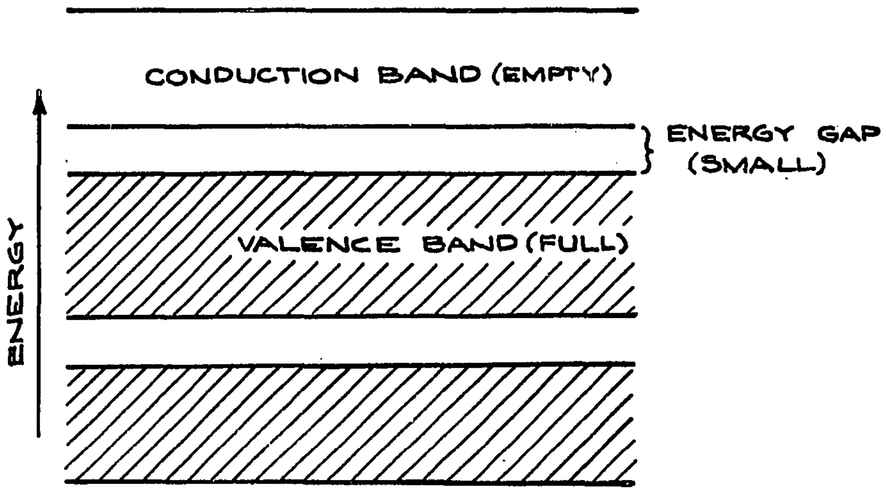
G_i = Number of available i states

The energy band structure is pictured in Figure II-2.

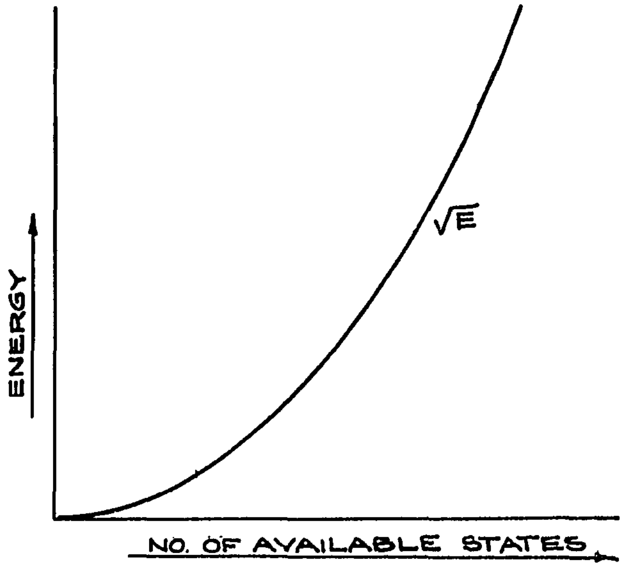
Figure II-2 as drawn must be modified as the temperature increases to include the effect previously noted:

$$\text{Fermi Probability of Occupation} = \frac{1}{1+e^{\frac{E_i - E_f}{kT}}} \qquad \text{eq. 7}$$

At absolute zero, electrons cannot take a very small



(a) BAND STRUCTURE



(b) RELATIVE AVAILABILITY OF STATES IN THE CONDUCTION BAND

FIG. II - 2 ENERGY BAND STRUCTURE OF A SEMICONDUCTOR AT ABSOLUTE ZERO energy change if they occupy a space in the uppermost completely filled band, because there is no nearby unoccupied state available. At higher temperatures, some electrons are in the heretofore empty band called the conduction band, and can assume large changes in addition to those very small changes in energy; vacant positions in the originally full "valence" band provide vacant energy levels for other electrons with nearly the same energy. The usual treatment develops the behavior of these vacancies which are known as "holes."

Introducing known impurities in the crystal structure provides electrons with an energy just under the lower level of the conduction band for "n" type conduction or vacancies just above the highest level of the valance band for "p" type conduction. The development usually continues with such treatment to develop the conduction characteristics of doped semiconductors, and junction behavior. This further development is, of course, important and not without bearing on surface behavior, but the review of conventional semiconductors will not be carried to completion.

It has been established that a definite gap in energy levels is a normal feature of the perfect crystalline semiconductor. Deliberate introduction of substitution impurities provides additional carriers which bring about "n" (electron) conduction or "p" (hole) conduction. In normal use any other energy levels which exist in the forbidden energy gap will provide some deterioration of performance.

Any imperfection in the crystal structure is likely to produce allowed energy levels in unwanted places. The most drastic change in the crystal structure occurs at the termination of the crystal at any surface. With an abrupt ending of silicon in a vacuum, no impurities are present to influence the energy level, yet an effect occurs. Tamm[1] devised a way of depicting the potential energy structure of a semi-infinite body terminating in a surface. See Figure I-b.

As in the infinite crystal lattice, rectangular approximations are used to permit a reasonably simple solution of the Schroedinger equation. The treatment outlined here is covered in relatively more detail in Reference 1.

The solution of ψ for negative x must contain an exponential decaying function in x. If it is assumed that the Bloch functions previously cited still satisfy ψ for $x > 0$, it is only necessary to match x and $\frac{d\psi}{dx}$ at $x = 0$. This should be possible with a combination of $\psi_1 = Ae^{ikx}$ and $\psi_2 = Be^{-ikx}$ since this provides two constants for two boundary conditions.

In the infinite case, K could not be imaginary or complex since $e^{\alpha x}$ (α = real) would become infinite at either $x = \infty$ or $x = -\infty$. In the semi-infinite case, an imaginary K is possible since the Bloch functions are defined only for positive x. Again considering the boundary conditions, Tamm

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[1] Tamm's approximation and solution is outlined in: Many, A., Y. Goldstein, and N.B. Grover, Semiconductor Surfaces. New York: John Wiley, 1965, pp 166-169.

concludes that there are additional energy levels, and that these lie in the forbidden band.

As Figure II-1b represents a chain of atoms terminating in a surface, it is expected there would be an energy level for each such terminal surface atom.

Since there are approximately 5×10^{22} silicon atoms in one cubic centimeter of silicon, there should be $(5 \times 10^{22})^{2/3} \approx 10^{15}$ atoms per square centimeter. This, then, is the expected density of unwanted energy states between the conduction band and the valence band for an abruptly terminated surface in a vacuum.

These energy levels, as well as any other energy levels in the forbidden band, whatever the origin, sometimes bear special names. An energy state well above the valence band, or deep below the conduction band, is often termed a "trapping state" or trap. When such states are occupied, they may have little effect of their own on the conduction process in the semiconductors, but because they represent one form of surface charge, they tend to attract mobile carriers, electrons or holes. These mobile carriers accumulated in the many atomic layers beneath the surface can bring about changes in the conduction pattern in the bulk near the surface. This will be discussed further when accumulation layers, inversion layers, and channels are discussed.

3. Arrhenius and Eyring Equations

If in deriving equation 6 the assumption that Pauli's exclusion principle is not made, a different type of statistics are generated, namely Maxwell-Boltzman. Instead of the Fermi factor, a factor similar to the following will result:

$$F_{MB} = e^{-\frac{E_i}{kT}} \qquad \text{eq. 8}$$

where: e = Napierian base, 2.718 . . .

E_i = Energy of the ith state

k = Boltzman's Constant

T = Temperature

It may also be noted that at high energy levels E_i, the Fermi Factor (eq. 7), behaves much as the Maxwell-Boltzman Factor, since if $E_i >> E_f$ and $E_i >> kT$ both E_f and the unity factor in the denominator of equation 7 can be ignored, resulting in the expression of equation 8.

The Arrhenius equation results if an assumption is made that for a chemical reaction to transpire it is necessary for the atoms, ions or molecules to have a certain minimum energy of activation before any reaction can transpire. The rate then would be proportional to the percentage of particles or molecules that possess an energy equal to or in excess of the energy of activation, E_a. As noted, if E_a is sufficiently high, the original statistical behavior of the particles is of little consequence.

The total number of molecules or particles is:

$$N = \int_0^\infty Ae^{-\frac{E}{kT}} dE$$

$$= kTA$$

And the activated number is:

$$N_A = \int_{E_A}^\infty Ae^{-\frac{E}{kT}} dE = kTAe^{-\frac{E_A}{kT}}$$

The percentage is thus:

$$\frac{N_A}{N} = \frac{-kTAe^{-\frac{E_A}{kT}}}{+kTA} = e^{-\frac{E_A}{kT}} \qquad \text{eq. 9}$$

Hence:

The rate, R, is proportional to $e^{-\frac{E_A}{kT}}$

Later in this outline the other factors which effect the rate of chemical reaction will be considered. For the present, the simplified assumption (that the rate is also proportional to the number of collisions per unit time in a given volume) serves to introduce another factor. The predominant effect, insofar as the Arrhenius equation is concerned is the absolute temperature

$$R \propto e^{-\frac{E_A}{kT}} \qquad \text{eq. 10}$$

$$\text{or } \ln R = \text{constant} - \frac{E_A}{kT} \qquad \text{eq. 10(a)}$$

In Chapter I the subject of accelerated life testing was introduced. If any stress factor is increased, the life will usually be shortened. This will be true whether the stress is electrical, mechanical, thermal or of any other nature. The Arrhenius equation illustrates why temperature is a stress that is widely used for accelerated life testing.

If a failure mode is due to a chemical reaction, or to any other phenomena that progresses in accord with Arrhenius equation, then

$$\frac{\text{Failure}}{\text{Unit Time}} = F \propto R \propto e^{-\frac{E_A}{kT}}$$

or

$$\ln F = \text{constant} - \frac{E_A}{kT}$$

A plot of $\ln F$ vs $\frac{1}{T}$ should result in a straight line with a negative slope. If a failure rate is extremely low at operating or storage temperature but measurable at higher temperature, several points can determine if the $\ln F$ vs $\frac{1}{T}$ is a straight line and, if so, an extrapolation of this line can be employed to determine the rate of failure under operating or storage conditions.

A few comments are in order regarding the pitfalls of this technique. In Chapter I, reference was made to Lewis and Boher (Chapter I, Reference 4) in connection with accelerated aging through elevated temperatures. Figure II-3 is taken from their article, and illustrates a device with two temperature dependent failure modes. At low temperature, the mode with lower energy of activation E_A' dominates, whereas at higher temperature the mode with the higher slope (higher E_A) is dominant. Any failure prediction based on the higher temperature range and extrapolated back to low temperature will result in predicting failure rates that are far too low. If one considers the extreme importance of very low failure rates in a system of 10^6 components, this is an important consideration.

Lewis also cites an example of another variety. In this instance, electrolytic action is taking place along a surface of a spiral resistor under power in a humid atmosphere. Hence, the metallic resistance film is removed from one side of the spiral and deposited on the other side of the spiral one turn away. This generates changing surface and changing resistance. Increasing temperature on such a surface may suddenly minimize the surface moisture content, and change or eliminate the mode of failure.

It is entirely reasonable that a third mechanism can take

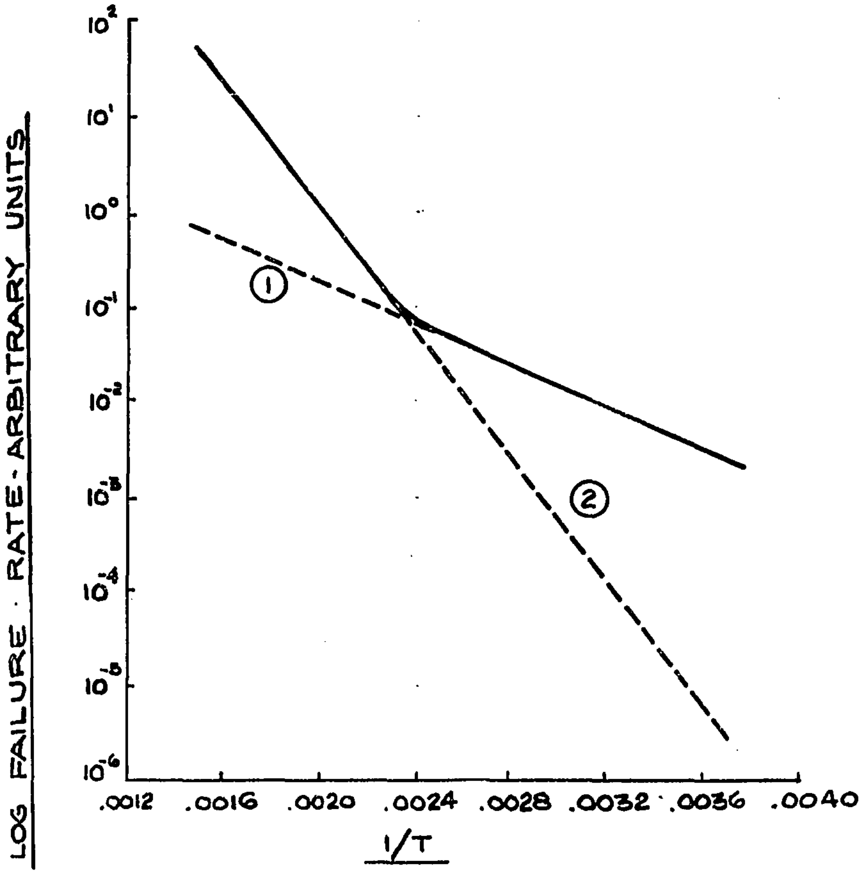

FIG II-3 A PLOT OF LN. F vs. 1/T FOR A DEVICE WITH TWO TEMPERATURE DEPENDENT FAILURE MODES. (FROM: LEWIS AND BOHER.)

place, namely the initiation of a mechanism by high temperature that would not occur at operating temperature. For example, every unit tested in Chapter IV consists of a silicon SCR or Diode chip, passivated with an oxide or nitride layer, in a composite of resin or glass encapsulation. Lead connections complete this conglomerate. The glass units, in particular, should be relatively slowly affected by moisture. It is easily visualized what might happen if the glass were lowered from higher temperature as the metallic leads will shrink relatively more leaving a fissure or a crack leading to the heart of the device. Moisture would very quickly saturate the silicon surfaces and failure rates or reverse current leakage rates might be cataloged as large compared to the true rate under conditions likely encountered by the component.

Eyring[2] devised an alternate to the "collision" theory of reaction which involved an intermediate state in equilibrium with the initial reactants. His result, using stress activated states gives a rate:

$$\text{Rate} = K = ATe^{-Eo/kT} \qquad \text{eq. (11)}$$

where: A contains the frequence of collision factors, and any stearic effects

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[2] Glasstone, S., K.J. Laidler, and H. Eyring, The Theory of Rate Processes, New York: McGraw-Hill, 1941.

E_o = energy of activation

k = Boltzman's constant. Note: There is no loss in generality if R (the gas constant) is used in place of k, providing the correct value of E_o is used. k is on a per molecule or atom basis. R is on a per mole basis.

It should be noted that for many practical cases, there is little difference between Arrhenius' and Eyring's equations. For a small range of temperatures, in that region of rapid change of the exponentional, the AT of Eyring may be considered a constant.

More recently,[3] some additional interest has evolved around a modified Eyring equation:

$$R = ATe^{-\frac{E_o}{kT}} \left[e^{\left(\left(C + \frac{D}{kT}\right) S\right)} \right] \qquad \text{eq. (12)}$$

where: T = temperature

E_o,D = activation energies

A,C = frequency factors

S = magnitude of non-thermal stress

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[3] Gorton, H.C. and K.P. Duchamp, "Research Toward a Physics of Aging of Silicon P-N Junctions", IEEE Transactions, Component Parts, CP-11, No. 1, March 1964, pp 28-32.

Once these constants E_o, D, A and C have been properly evaluated, this would clearly be an improvement for calculating non-accelerated failure rates.

4. Diffusion

Considerable time has been devoted in discussing the rate equations with little or no emphasis placed on why the relationships are so important in considering the semiconductor surface. Many chemical reactions are deliberately employed in the formation of protective films. Data will be displayed in Chapter III that illustrates differences in film properties due to changes in the method of preparation. Kinetic information is valuable. The completed assembly invariably has some small quantity of contaminating material in the final enclosure. This may be contained in that gaseous space encapsulated under the glass, or in solid form as part of the plastic or resin envelope. Reaction of these contaminants can modify the surface and contribute to the leakage.

Overshadowing and also supplementing all of these chemical reactions is the process of diffusion. The diffusion coefficient, D, which will be defined shortly, depends on temperature in the manner of a true rate equation. Arrhenius' euqation or Eyring's equation can be used to predict the change in the diffusion coefficient with temperature, if the activation energies are known.

Diffusion must be considered in the preparation of semiconductor devices and in predicting their reliability. The operation of a conventional transistor depends on the diffusion of holes or electrons to sweep minority carriers through the base region by virtue of a concentration gradient that is established when the emitter-base junction is forward biased.

The collisions of atomic or molecular particles can lead to chemical reactions. When two unlike materials are brought together, such reactions will take place more readily in those regions where the concentrations of both reaching constituents is high enough to favor collision of one molecule with a molecule of the other constituent. The diffusion equations are used to predict the rate at which the concentration of one constituent changes with time throughout the second material. In gases and liquids convection or mechanical mixing may complicate the process. The diffusion rates of a solid may be 6 to 9 order of magnitude smaller than the rates in a gas. The rates in a solid may vary over a considerably greater range than rates in a gas, depending on the binding forces of the particular solid. For the case in point, the diffusion of sodium ions in silicon nitride and silicon dioxide differ by a factor of 10^{10} (See Chapter III). A derivation of Fick's first law is accomplished by considering the random motion of a component by Gibbons.[4] A kinetic approach for the

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[4] Gibbons, James F. Semiconductor Electronics. New York: McGraw-Hill, 1966.

temperature dependence of the diffusion constant "D" may be found in a treatment by Boltaks.[5] Energy level treatments are developed in texts by Jost[6] and Glasstone, Laidler and Eyring.

Fick's first law in one dimension is:

$$J_x = - D\frac{\partial N}{\partial x}$$

where: J_x = Diffusion rate in particles per square cm per second.

D = Diffusion coefficient

N = Particles being diffused per cubic cm

x = Distance in cm

Fick's second law is:

$$\frac{\partial N}{\partial t} = \frac{D\partial^2 N}{\partial x^2} \qquad \text{eq. (14)}$$

The diffusion coefficient is temperature dependent:

$$D = D_o e^{-\frac{E_A}{kT}} \qquad \text{eq. (15)}$$

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[5] Boltaks, B.K., Diffusion in Semiconductors. New York: Academic Press, 1963.

[6] Jost, W., Diffusion in Solids, Liquids, Gases. New York: Academic Press, 1960.

or according to Eyring:

$$D = CTe^{-\frac{E_A}{kT}} \qquad \text{eq. (15a)}$$

Equation 13 is useful for calculations involving known concentration gradients. An example would be the concentration of minority carriers in the base region of a transistor. Under many bias conditions $\frac{dn}{dx}$ is a constant providing an easy solution to the minority carrier current. Equation (14) is applicable to those cases involving diffusion of deliberate or unwanted impurities through insulation, or into silicon. The diffusion coefficient is related to the mobility of particles and the flow of charged particles through a medium when an electric field is applied is dependent on D_o. Forced diffusion modifies equation (13) and (14), but this is not explored further here.

Solutions to the diffusion equations are listed in closed form for many types of boundary conditions in reference 5. These solutions are not repeated here.

A feature of the silicon-insulator system that is explored in Chapter II is the capability of developing extreme temperature differences in the insulator and the silicon by rapid absorption of infra-red energy of a particular wavelength. This may create some use for still another facet of diffusion:

Gases, liquids and solids exhibit a property when a thermal gradient is applied known as thermal diffusion. Another term applied to this same effect is partial demixing. It was first observed experimentally in liquids in 1856. Lighter particles or molecules tend to concentrate in the higher temperature region and heavier particles or molecules gather in the lower temperature region.

5. Methods of Layer Formation

The diffusion of any type of molecule through a substance depends on both the diffusing molecule and substance in which it is diffusing. There is evidence to show that diffusion occurs easily at the crystal boundaries of a polycrystalline material. The behavior of silicon nitride as a barrier to sodium diffusion is discussed in Chapter III. Figure III-3 illustrates the increased diffusion for large crystalites. If the structure of the individual crystals is such that diffusion is greatly impaired, then the data shows clearly that structure is all important in relation to diffusion. To this writer's knowledge, there have been no direct measurements of diffusion in single crystal silicon nitride, but the literature is cited in Chapter III for other types of inter-granular boundary diffusion.

Without any proof, the writer also cites the strong possibility that the number of surface "states" available in the silicon forbidden bands is strongly structure dependent. Practically speaking, the type of structure formed will be influenced, at least to some extent, by the method, rate, and other parameters of formation. Important dielectric difference of properties are documented in Chapter III. Even density difference occurs.

Many of the methods of formation of passivating layers on silicon are covered in some detail for silicon dioxide by Burger and Donovan[7] in the second chapter of their book. This dissertation will summarize the methods shown therein, with a few additions:

(A). Direct oxidation of silicon. This can be accomplished in a high temperature atmosphere of air, wet air, oxygen, wet oxygen or steam. The growth rate is influenced by the method and by the temperature. Each method has unique problems. It is not believed that the final structure is vitally effected by the oxidation media used, although there is evidence that the "surface states" of the $Si-SiO_2$ interface are influenced favorably by the presence of moisture during oxidation. Certainly the high formation temperature involved (approximately 1150°C) in combination with other physical properties will result in a stressed film when cooled to room temperature. This is discussed in more detail in Chapter III.

The rate of oxidation is dependent on temperature, partial pressure of H_2O, partial pressure of oxygen, and type of

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[7] Burger, R.M. and R.P. Donovan, Silicon Integrated Device Technology, Volume 1. Englewood Cliffs, New Jersey: Prentice Hall, 1967.

carrier gas, if any. These rates are discussed in detail in reference 7. A single point is included here for an order of magnitude approximation. In dry oxygen, at one atmosphere at 1000°C, a 1000 Å film is formed in 100 minutes.

A side comment is in order here. Frieser[8] attempted an equivalent process for forming silicon nitride, namely heating silicon at a high temperature in a nitrogen atmosphere. The results were visibly polycrystalline in form. This resulting poor film is not totally unexpected. It has been determined experimentally (see Table 1, Chapter III) that the rate of diffusion of sodium in silicon nitride differs from that rate of diffusion of sodium in silicon dioxide by a very large factor (10^{10}). The relative size of nitrogen ions to sodium ions is in the ratio of 1.71 to 0.95 , respectively. On this basis, it is expected diffusion of nitrogen through a layer of amorphous silicon nitride would be very small. By the same reasoning, diffusion of silicon would be expected to be low. The growth could then only proceed with some other arrangement for supplying new reactants. Diffusion along crystallite boundries could possibly be that mechanism. This is consistant with the photographs of Frieser's film.

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[8] Frieser, R.G. "Direct Nitridation of Silicon Substrates", <u>Journal of the Electrochemical Society</u>, Vol. 115, No. 10, October 1968, 1092-1094.

(B). Evaporation. This is applicable to most films except silicon nitride which tends to decompose at high temperature. In evaporation the starting material may be of high purity, but at the evaporation temperature, some thought must be given to the possibility of contamination evolved by the boat or filament, or perhaps a sharing of oxygen with the boat with a subsequent reduction of the material being evaporated. Even the slightest reduction of the material being evaporated may have an adverse physical effect on devices of the future. The silicon substrate can be much cooler in this process than the substrate during direct oxidation.

(C). Ion Bombardment Sputtering. In this technique inert gas (e.g., argon) ions are accelerated into a target of the element or compound to be deposited which in turn travels to the silicon substrate. Sources of impurity might be the inert gas supply system or any secondary surfaces with which ions, electrons, or molecules might collide.

Variations of this process include DC sputtering, RF sputtering, the presence of magnetic fields to direct the beams, and various electrode arrangements.

(D). Reactive Sputtering. This is similar to the previous process, except that an active gas is introduced to react with molecules of pure silicon bombarded free of the target. This is a method of applying silicon nitride. In processes B, C, and D, the films can be deposited at relatively low temperatures. Substrate cooling could provide even closer controls.

(E). Chemical Vapor Deposition. (pyrolytic decomposition) Silicon nitride, silicon dioxide, aluminum oxide and titanium oxide are among films deposited by this technique. A reaction mixture, typically hydrogen, silicon tetrachloride, and water vapor, is allowed to contact heated silicon. The resulting chemical decomposition results in an SiO_2 layer on the substrate. This method contrasts with direct oxidation in that it is not necessary for oxygen to diffuse through the layer for continuation of the process. Since both processes are carried out at relatively high temperatures, both should have highly stressed films at room temperature. However, successful chemical depositions have been made at temperatures as low as 350°C by V. Y. Doo.[9]

A separate class of chemical depositions is possible by utilizing organic compounds containing silicon or aluminum and decomposing them in an oxidizing atmosphere. Any carbon or hydrogen present is oxidized leaving only SiO_2 or Al_2O_3.

(F). Anodizing. Electrolytic capacitors have a long history of successful formation of aluminum oxide and tantalum

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[9] Doo, V.Y., D.W. Boss, R. Valletta, and W.A. Pliskin, "Chemical Vapor Deposition of Oxides and Glasses", Extended Abstracts of the Electrochemical Society Spring Meeting, New York, New York, May 4-9, 1969, Abstract No. 42, pp 106-110.

oxide films. Since aluminum can be easily and directly deposited on silicon by evaporation, this technique might be considered more or less seriously as a possible protective coating. The process involves electrolytically oxidizing the aluminum forming a very thin film at essentially room temperature. Purity is a problem. Further in the case of a semiconductor, the aluminum would have to be totally consumed near a junction, or the aluminum might subsequently diffuse into the silicon surface and act as a doping element.

Silicon can also be anodized to some extent in liquids or ionized gases.

(G). Electron Beam Evaporation. An intense electron beam will evaporate most refractory materials. A special difficulty is imposed with normally insulating materials, since charge accumulation would soon spoil the beam. Hence, some auxiliary arrangement to pre-heat the insulating-material is required. Heating the insulator to a high temperature will significantly increase its conduction. The technique is similar to evaporation but without requiring the use of a boat of filament.

(H). CO_2 Laser Beam Evaporation. Based on the high absorptivity by silicon dioxide of radiation of the CO_2 Laser (10.5μ) experimentation was undertaken to evaporate silica and alumina directly on a silicon substrate. The CO_2 Laser beam is introduced into the vacuum system through a polished crystal of potassium chloride. Focusing this beam produces intense heat in the silica. The coefficients of absorption at a wavelength of 10.5 microns of aluminum oxide and silicon monoxide are both very high. A development in a later chapter also indicates a possibility of utilizing silicon nitride with this technique. This method should be much simpler than the electron beam evaporation, and could be done in a very high vacuum prociding the possibility of depositing films of high purity. The elimination of the necessity of using a hot filament or inert gas should provide purer films. Independent experiments along these lines have been conducted by G. Hass and J. B. Ramsey.[10] Their interest was in optical coatings.

This technique, as well as any evaporation technique, undergoes "shadowing" if any surface irregularities exist.

(I). Sedimentation. A relatively recent adaptation from the ceramic industry is film formation through sedimentation. In the process described by Dumensil[11] a glass is smelted, ground, suspended in a liquid, and sorted to particle

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[10] Hass, G. and J.B. Ramsey, "Vacuum Deposition of Dielectric and Semiconductor Films by a CO_2 Laser," Applied Optics, June 1969, pp 1115-1118.

[11] Dumensil, Maurice and Robert Hewitt, "Some Recent Developments in Fused Glass on Semiconductor Devices," Extended Abstracts of the Electrochemical Society Spring Meeting, New York, May 4-9, 1969, Abstract No. 41, pp 103-105.

sizes of approximately one micron. The suspension is allowed or forced to deposit on a silicon substrate which is subsequently fired. The advantages attributed to this technique include the ability to minimize sodium content and diffusion and to form uniform coatings of low melting glasses. Dumensil describes several glasses which are suitable for this purpose. This method might include the commercial glasses exemplified by Corning 7723, with a softening point of 770°C. The coefficient of expansion of this glass is 3.5×10^{-6}; its resistivity is 10^{12} ohn/cm; and its dielectric constant is 5.86.

Each of the above methods attempts to achieve an amorphous film. In the case of the direct nitriding of silicon, the resulting film was noted to be polycrystalline. Crystalline structures of any appreciable size in aluminum oxide and tantalum oxide films have been associated with the failures of electrolytic capacitors, and we anticipate that the same will hold true for silicon insulating layers. Dzimianski[12], et. al., point out that even with the best commercial technology, some crystallinity is bound to occur. They further reference the known occurrence of selective diffusion along crystalline interfaces.

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[12] Dzimianski, J.W., E.R. Pemsel, W.J. Lytle, and S.M. Skinner, "Silicon Surface Passivation: Materials and Microproperties," Physics of Failure in Electronics, Vol. III, Rome Air Development Center, April 1965.

Crystalline structure is often enhanced by high temperature, slow cooling rates, slow depositions, the presence of H_2O vapor, impurities, and by utilizing a substrate with the same crystal form as the insulating layer. Most investigators choose an arbitrary size of polycrystalline structure as the dividing line between "polycrystalline" and amorphous material. An average crystal size of 50 Å might be a good demarcation.

Future methods of forming films or treating present films will evolve. Already heat treating of films has been used experimentally with favorable results. Perhaps more futuristic is the possibility of treating films with neutron irradiation. Primak and Kempwirth[13] report a decrease in volume of 2.7% for silicon dioxide when placed near the fuel in a nuclear reactor.

6. Structural Rules[14]

Ceramic engineers, glass chemists, and physical chemists

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[13] Primak, William and Robert Kompwirtz, "Ionization Expansion of Pile Exposed Vitreous Silica," Journal of Applied Physics, Vol. 40, No. 6, May 1969, pp 2565-2570.

[14] This section is included in this dissertation primarily to raise the speculative possibility that some of these structural concepts may be useful in predicting quantitative electrical properties or other physical phenomena which relate directly to the electrical behavior of semiconductors. These speculations are not included in the summary or conclusions of this dissertation, nor are they necessary for the further developments of chapters beyond Chapter II. (next page)

have obtained information concerning the structure of films which relates to their electrical properties and which provides some insight in the process of diffusion. Some of the empirical rules developed are listed below. Eventually additional work may be performed in this area which relates the film properties, stoichiometry and the method and conditions of formation. One structural occurrence that is of interest is the sharp increase in the diffusion coefficient, D, for sodium in a silicon nitride film when even a small percentage of silicon dioxide is present in the film.

It is assumed that there is no necessity to describe covalent bonds or ionic bonds. The crystalline or amorphous structure of potentially useful film substances is of particular interest. Silicon dioxide is a good example of a material which may take many forms. Crystalline silicon dioxide may exist as α quartz, β quartz, and various cristobalite and tridymite forms. To be sure, these are not

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[14] (continued) For example, sodium diffuses many orders of magnitude more freely in silicon dioxide than in silicon nitride. The difference in electronegativity of silicon and nitrogen is 1.1, whereas the difference between silicon and oxygen is 1.7. From Figure II-4, it might be expected that the bonds silicon dioxide are therefore approximately 50% ionic, and in silicon nitride approximately 20% ionic. In an amorphous film some short-range structure is almost always observed by X-ray diffraction. The question this writer poses is: Does the higher percentage of ionic bonds cause the short-range structure in silicon dioxide to behave like the transition region between crystallites of polycrystalline SiO_2? It is well known that diffusion occurs readily along grain boundaries, and it would follow that diffusion would occur easily in any material with structural similarities to such boundary regions.

necessarily all stable forms at room temperature, but since the temperature of formation of films for semiconductor use is around 1100°C, there is the possibility of the existence of several of these forms. Usually the SiO_2 films formed are amorphous. That is, without long-range crystallinity and probably to some extent they resemble glass. Both fused silica and SiO_2 films formed by oxidation do not have long-range crystalline structure.

Pauling[15, 16] developed rules which describe the "minimum energy" grouping of anions around a cation which predict the structure of the basid polyhedron of the compound. A crystal of glass is formed by combinations of such polyhedra. He also derived, from the binding forces on various atoms, the concept of electronegativity in which, as one might expect, the usual anions -- fluorine, oxygen and the like were most "electronegative" than say, silicon -- which is, in turn, more "electronegative" than aluminum. This concept can then be used to estimate the relative percentage of ionic bonds vs. those of co-valent nature.

Table 1 shows the ionic crystal radii and the electronegativity of several elements of interest:

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[15] Kingery, W.D., Introduction to Ceramics. New York: John Wiley, 1960.

[16] Pauling, Linus, The Nature of the Chemical Bond. Ithaca, New York: Cornell University Press, 1940.

TABLE 1

	Ionic Crystal Radii	Electronegativity
Si^{4+}	0.41	1.9
O^{2-}	1.40	3.6
N^{3-}	1.71	3.0
Al^{3+}	0.20	1.6
Be^{2+}	0.31	1.3
F^{-}	1.36	4.0

Table 2 defines the "coordination number" based on the ratio of cation radius to anion radius, and describes the "probable" basic polyhedra:

TABLE 2

Coordination No.	Grouping Around Cation	Radius Ratio
8	corners of cube	1.000-0.732
6	corners of octahedron	0.732-0.414
4	corners of tetrahedron	0.414-0.215
3	corners of triangle	0.225-0.155
2	linear	0.155-0.000

Figure II-4 shows an estimate of the fraction percentage of ionic bonds.

Pauling's empirical rules for crystals are listed:

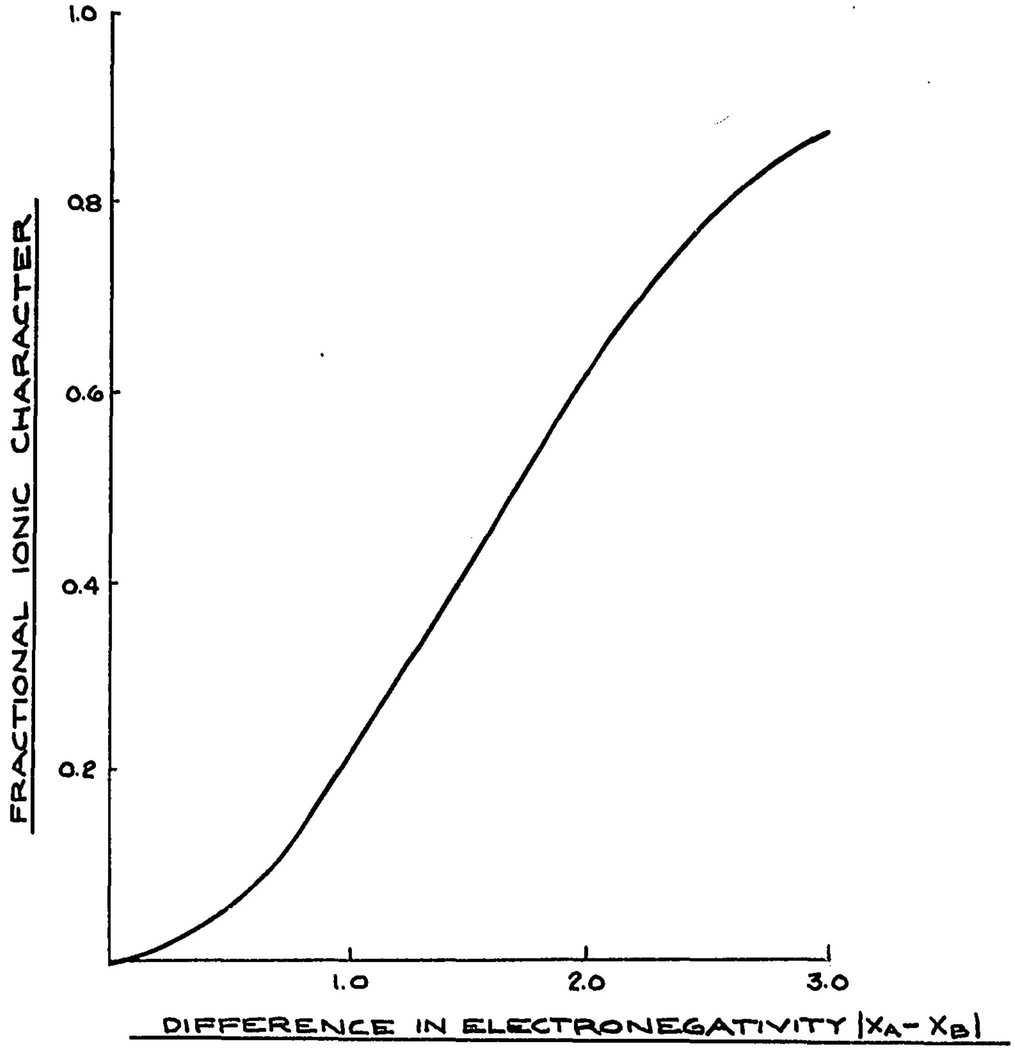


FIG II - 4 A PLOT OF EXPECTED PERCENTAGE OF IONIC BONDS VS. THE DIFFERENCE IN ELECTRONEGATIVITY OF THE ANION AND CATION (AFTER: KINGERY)

1. The coordination number is determined by the geometry required for anions and cations to remain in contact.

2. The existence of faces or edges common to two polyhedra decreases the structure's stability.

3. Charge neutrality is necessary for the totality of bonds associated with each anion and cation.

4. In crystals containing different cations those of high valence and low coordination number tend not to share polyhedral elements with each other.

5. The number of essentially different kinds of constituents tends to be small.

Zachariasen's rules for oxide glasses (following) may be compared with Pauling's rules:

1. Each oxygen ion should be linked to not more than two cations.

2. The coordination number must be small ($<$ 4).

3. Oxygen polyhedra can share corners but not edges or faces.

4. At least three corners of each polyhedron should be shared.

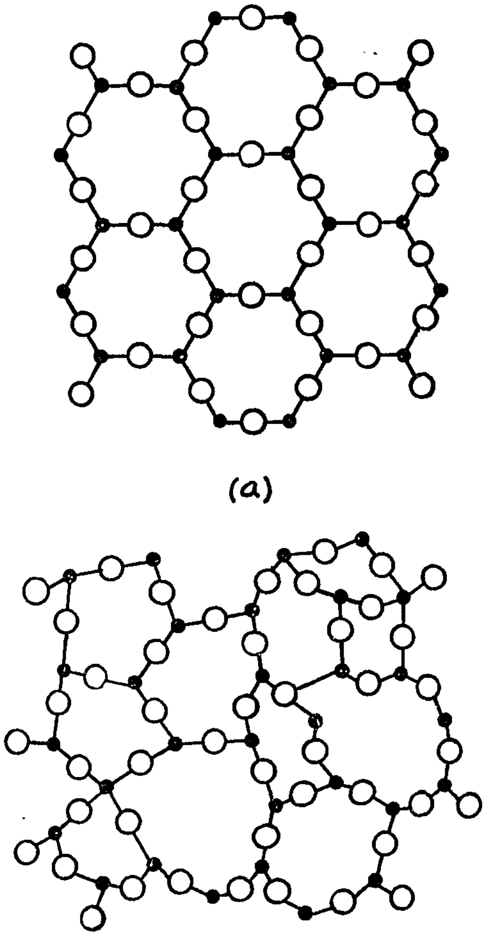
It is of interest to note that in the theory of glass formation, B. E. Warren depicts a sodium silicate glass as having a basic matrix or chain of -Si-0- combinations with the sodium more or less in the open spaces. Hence, we may speculate on the possibility that sodium migrates more freely under such an arrangement.

Two figures are included from Kingery which depict a two-dimensional crystalline lattice compared with the irregular glassy network. See Figures II-5 and II-6.

A third figure from Kingery attributed to Warren shows how sodium ions might fit into the openings in the network. It is conceivable that a small quantity of Na ions could fit in without expanding the basic network, and the binding forces on the sodium might be very loose. It may be significant to determine whether or not a "glass" type structure is possible for such a non-oxide compound as silicon nitride in an amorphous state.

7. Accumulation Layers, Inversion Layers, Channels

Earlier in this chapter, the existence of energy levels in the forbidden band (between the valence band and the conduction band) was attributed to trapped carriers at the surface of the semiconductor. Trapped carriers also represent electrical charge which is fixed at the surface so long as the carriers remain immobilized by the occupation of such energy



(a)

(b)

FIG. II-5 COMPARISON (a) TWO DIMENSIONAL CRYSTALLINE LATTICE AND (b) GLASSY NETWORK. (AFTER: ZACHARIASEN AND WARREN)

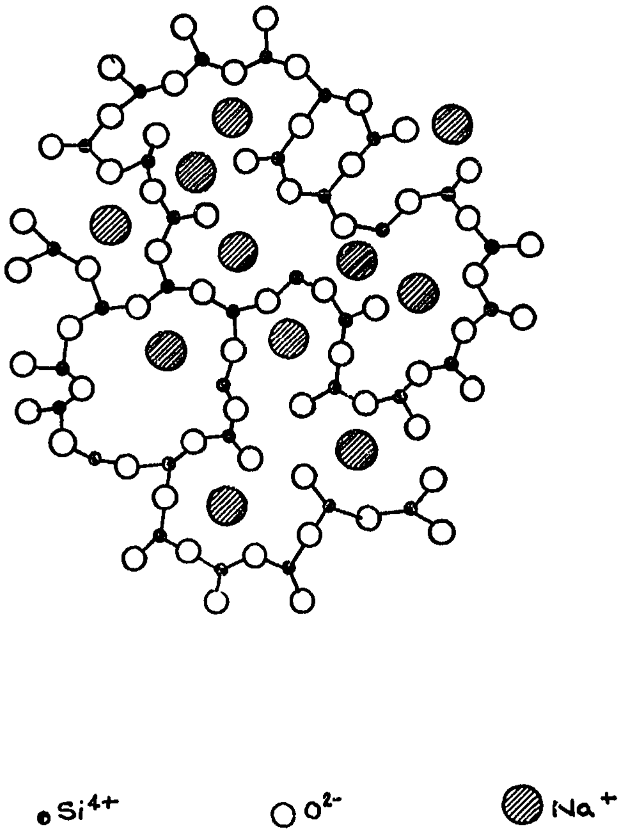
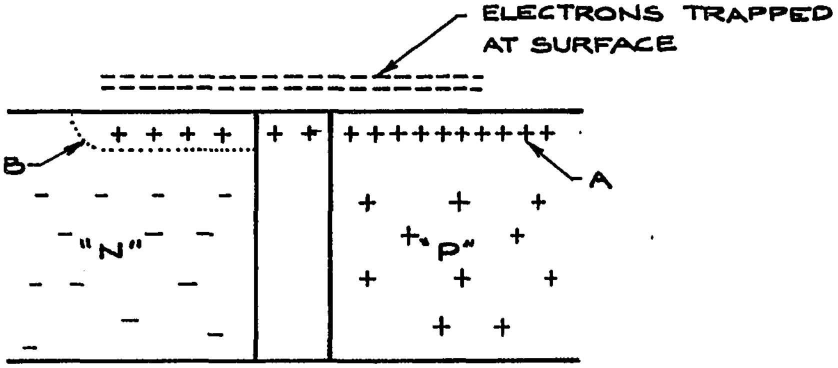


FIG. II- 6 A GLASSY NETWORK CONTAINING SODIUM. (AFTER: WARREN) states. If, for example, electrons are trapped, a negative charge exists at the surface. This charge, in turn, produces a field that attracts mobile carriers of the opposite sign, in this case holes, to the region of the surface.

From a simplified viewpoint, if additional mobile carriers are present in any volume of the material, these carriers are able to conduct and resemble the carriers formed from group III or group V substitution elements. If holes are attracted to the surface, and the material is already "p" conductivity type, a layer of more highly conductive "p" material or an accumulation layer is formed.

If, on the other hand, holes are attracted to the surface of normally "n" type material, the excess holes suppress the number of available electron carriers and the region near the surface becomes less conductive. If additional electrons are trapped, the number of mobile holes may become greater than the number of electrons just under the surface, and for a short distance into the surface the layer may be "p" in nature. When this occurs, inversion is said to have taken place, and the layer is known as an inversion layer.

The inversion layers are usually quite thin and have little effect on the bulk conduction of any device. When an inversion layer bridges what would have been a normal junction, a "channel" is said to exist. An illustration of an inversion layer, an accumulation layer, and a channel is presented in Figure II-7.



(A) - ACCUMULATION LAYER WITH A LARGE EXCESS OF POSITIVE CARRIERS

(B) - AN INVERSION LAYER WHICH IN THIS CASE ALSO FORMS A CHANNEL

FIG. II-7 THE EFFECT OF TRAPPED ELECTRONS ON THE CONDUCTIVITY OF THE NEAR-SURFACE

If a channel bridges two junctions, as in a transistor, severe leakage can occur along this sub-surface. The exploitation of such channels, formed deliberately with applied fields, constitutes the conduction in a field effect transistor.

When positive charge is trapped at the surface, the same event occurs, but with electrons drawn to the under-surface, and the greatest effect on the "p" region under-surface.

Even in a diode, channels are undesirable. Direct surface conduction does not occur unless the channel extends from the junction to the opposite electrode, but the p-n junction area may be increased. The reverse current leakage is proportional to the junction area, and would be increased in such a case.

For introductory purposes, trapped carriers at the surface were depicted as a cause of attraction of holes or electrons to the surface. Any other form of charge which can create a surface field, including applied fields, can attract carriers and bring about this mechanism, or aid or oppose other field producing effects in creating accumulation or inversion layers.

When, for example, an oxide surface is grown, a fixed interface charge is found to exist. This charge is dependent on the orientation of the silicon, the method of growth and the extent of any post growth annealing operations. It is evident that such charge will participate in attracting carriers within the silicon. The work function differences in silicon, any protective layer, and any subsequent layer also effect the relative attraction of carriers.

8. MOS Devices[17]

In field effect transistors, the insulation separates the gate electrode from the surface of the semiconductor. The gate voltage applied determines the extent of the inversion and the resulting channel constitutes the normal conduction of this device. The metal-oxide-semiconductor (MOS) and metal-insulator-semiconductor sandwich make a very good investigative tool for many of the effects of inversion layers. These sandwiches also serve to explain some of the mechanisms that take place involving inversion. The treatment in this section reflects articles and talks by Goetzberger[18] and a review article by Snow and Deal.[19]

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[17] MOS devices are introduced both because of their extensive use as a device for film investigations, and because the MOS sandwich is the heart of one type of field-effect transistor. Many of the comments made about diode passivating layers will also apply to these devices.

[18] Nicollian, E.H. and A. Goetzberger, "Lateral A.C. Current Flow Model for Metal-Insulator-Semiconductor Capacitors." IEEE Transactions on Electron Devices, Vol. ED-12, March 1965, 108-117.

[19] Snow, E.H. and B.E. Deal, "Polarization Effects in Insulating Films on Silicon - A Review," Transactions of the Metallurgical Society of AIME, Vol. 242, March 1968, 512-523.

If a gate electrode is varied from a high positive potential to a negative potential over an "n" type semiconductor, the following sequence (with changing voltage) occurs: At a high positive potential, electrons are attracted to the silicon surface, and an accumulation layer is formed. Under this condition the capacitance measured reflects only the oxide layer. As the voltage is decreased, and finally made negative, the surface becomes depleted and the near surface silicon approaches the characteristics of an insulator. The capacitance of the silicon so depleted is in series with the normal insulation capacitance. The net result is a decreasing capacitance until full inversion is reached.

Various mechanisms affecting charge and polarization will influence the shape of the voltage vs. capacity curves. As an example, it is known that in oxide films sodium ions migrate readily to the oxide silicon interface under the application of positive bias to the gate electrode. These positive ions will tend to hold a built-in accumulation layer which will prevent inversion (hence capacitance loss) until a voltage is reached that is more negative than in the case of the same device prior to the migration of the sodium.

A similar accumulation effect is evidenced with polarization, and an opposite (depletion) effect is attributed to trapping of majority carriers in the silicon oxide interface.

9. Voltage Breakdown

Voltage breakdown in insulating layers may be influenced by a number of factors in thin films. Of primary importance are any defects or inhomogeneities in the insulating film. Under the high fields encountered in semiconductors: porosity, impurities, surface irregularities, and similar occurrences involving variations in dielectric constant can cause field concentrations that may greatly shorten the life or maximum voltage that a film can withstand.

The importance of these factors has a profound influence on the care and conditions necessary to produce insulating layers. Ultra cleanliness of every vessel, material or reagent is required. A grain of dust, dirt or organism of microscopic or sub-microscopic dimension could be the direct cause of failure of an otherwise flawless film.

The nature of breakdown in a solid, aside from the above features, is a very complex phenomenon dependent on temperature, field strength, thickness of sample, area of the electrodes, the nature of the electrodes, time, and probably many other parameters. Many investigators believe the ultimate breakdown to be a thermal phenomenon with increasing electric field ultimately causing more current to flow without further increase in E. This energy is dissipated as thermal energy and breakdown results when the increase in thermal energy lowers the resistance progressively with no further increase in applied voltage.

A second possibility involves a sudden onrush of current due to avalanche which may in turn be caused by inherent weak spots or perhaps may be just a statistical occurrence for a given relatively high field through the insulator. Breakdown of this nature is generally very localized. Differing theories explain why the material reaches the point of degradation. This material is summarized by O'Dwyer[20] and Klein[21] and will not be repeated here. Two points are of interest, however. First, the breakdown field strengths are much higher in very thin films. This leads to the practice of stressing these films to a degree which could not be tolerated in bulk insulating material. This leads to the second point of interest, in that if extreme uniformity is not achieved, weak areas will occur that will be subject to avalanche or thermal breakdown. Such non-uniformity could occur as a result of surface preparation, occlusion of impurities, or large crystallite structure formation.

10. Conduction in Insulating Films

The interest in insulating films in this dissertation will be confined to amorphous or nearly amorphous films.

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[20] O'Dwyer, J.J., "Theory of Dielectric Breakdown in Solids", Journal of the Electrochemical Society, Vol. 116, No. 2, February 1969, 239-241.

[21] Klein, N. "Electrical Breakdown in Thin Dielectric Films." Jour. of the Electrochemical Society, V. 116, N. 7, July 1969,963-972.

Crystalline films or polycrystalline films with large crystallites have other drawbacks. It is advantageous, however, to start from the concept of a uniform crystalline structure with its definite energy band structure, and speculate on the nature of energy bands when short-range order is substituted for the infinite series of potential energy wells hypothesized earlier in this chapter. The chief difference, according to Jonscher[22], is the absence of well defined valence and conduction bands, and the substitution of localized conduction and trapping states, as shown in Figure II-8.

At room temperature, thermal activation, together with band bending due to high field stresses combine to bring about a series of transitions from nearby energy states, each of which constitutes tunneling or moving of charge. Figure II-9 shows a plot of the logarithmic current vs. the square root of the applied voltage for a 3800 Å film of silicon monoxide. The major straight portion of the curve fits the equations of Poole-Frenkel emission or Schottky emission. The concern here is with the approximate film conductivity behavior, and not with the specific mechanism of conduction through the film. The fact that conductivity increases greatly with applied field helps to support a thesis that in a composite structure the current will tend to take a short path to the surface if there exists a mechanism for conduction along the surface.

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[22] Jonscher, A.K. "Electronic Conduction in Dielectric Films," pages 3-42 in Fredrick Vratny, Thin Film Dielectrics, Dielectrics and Insulation Div., Electrochemical Society, New York, 1969.

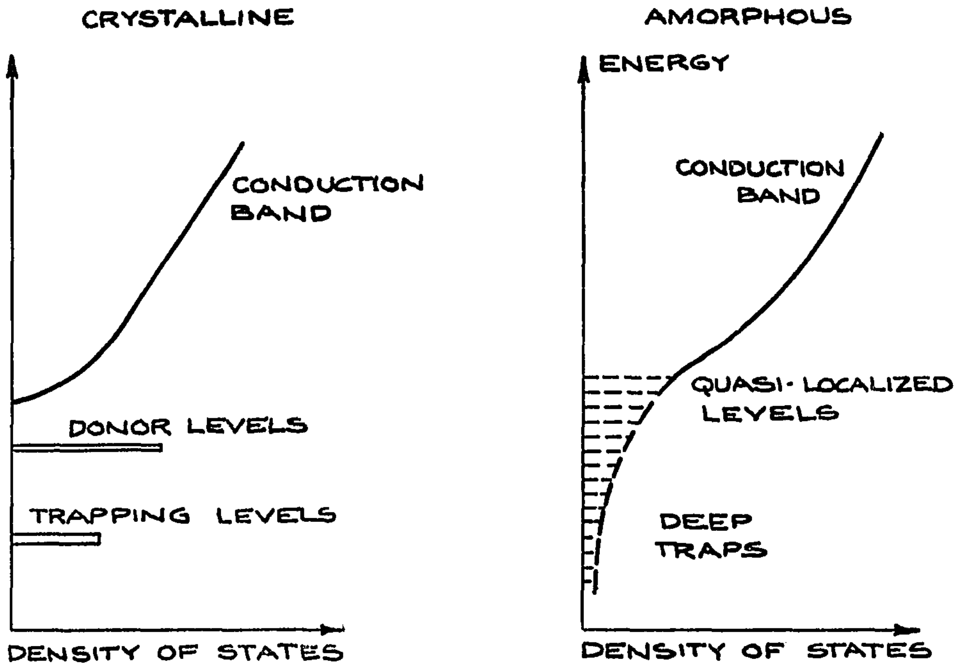

FIG. II-8, LOCALIZED CONDUCTION AND TRAPPING STATES IN A CRYSTALLINE AND IN A NON-CRYSTALLINE INSULATING SOLID

(AFTER: JONSCHER)

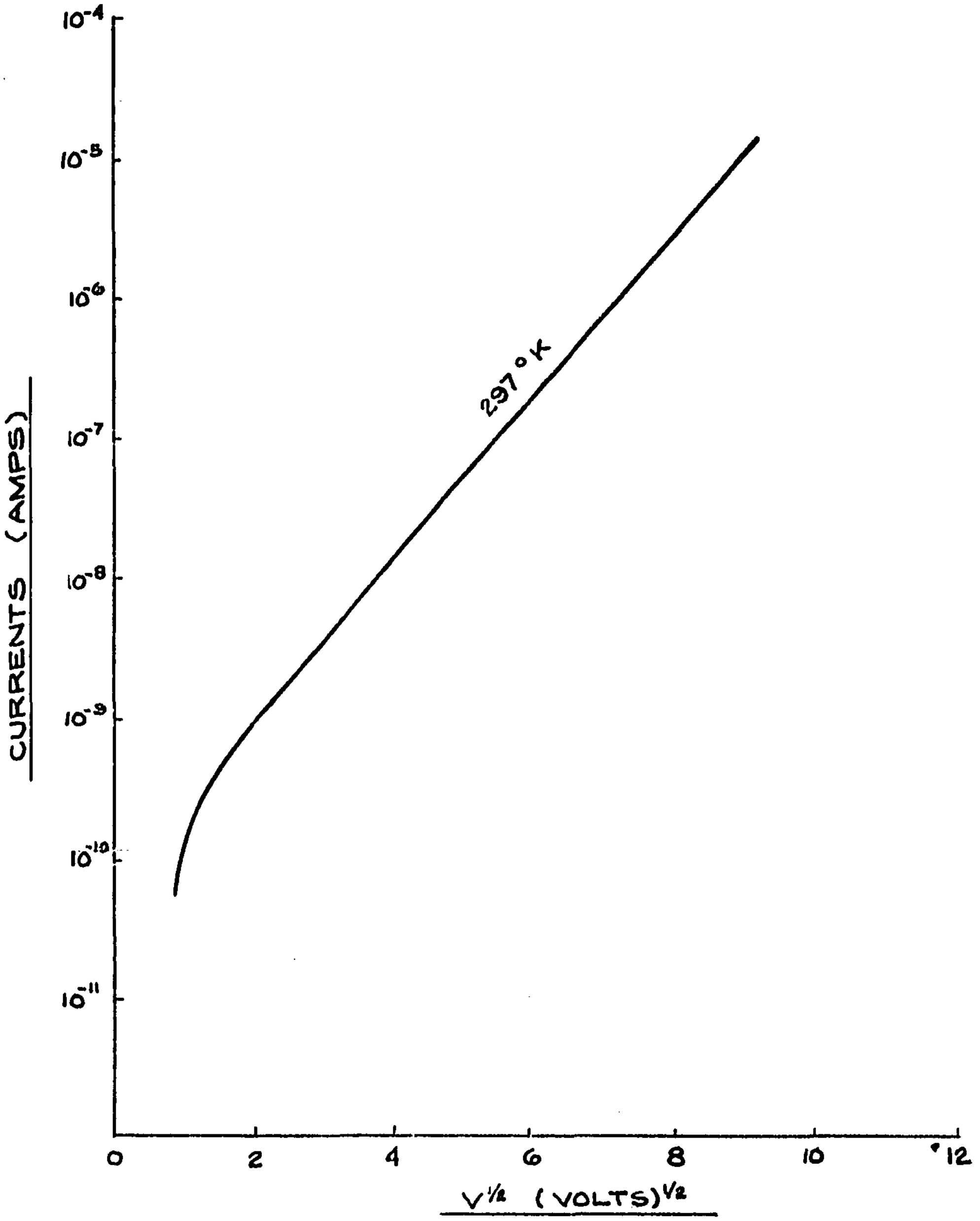

FIG. II- 9 PLOT OF VOLTAGE - CURRENT CHARACTERISTICS OF EVAPORATED SILICON MONOXIDE. (AFTER JONSCHER)

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[10] Hass, G. and J.B. Ramsey, "Vacuum Deposition of Dielectric and Semiconductor Films by a CO_2 Laser", Applied Optics, June 1969, pp 1115-1118.

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[12] Dzimianski, J.W., E.R. Pemsel, W.J. Lytle, and S.M. Skinner, "Silicon Surface Passivation: Materials and Microproperties," Physics of Failure in Electronics, Vol. III, Rome Air Development Center, April 1965.

[13] Primak, William and Robert Kompwirtz, "Ionization Expansion of Pile Exposed Vitreous Silica," Journal of Applied Physics, Vol. 40, No. 6, May 1969, pp 2565-2570.

[15] Kingery, W.D., Introduction to Ceramics. New York: John Wiley, 1960.

[16] Pauling, Linus, The Nature of the Chemical Bond. Ithaca, New York: Cornell University Press, 1940.

[17] MOS devices are introduced both because of their extensive use as a device for film investigations, and because the MOS sandwich is the heart of one type of field-effect transistor. Many of the comments made about diode passivating layers will also apply to these devices.

[18] Nicollian, E.H. and A. Goetzberger, "Lateral A.C. Current Flow Model for Metal-Insulator-Semiconductor Capacitors." IEEE Transactions on Electron Devices, Vol. ED-12, March 1965, 108-117.

[19] Snow, E.H. and B.E. Deal, "Polarization Effects in Insulating Films on Silicon - A Review," Transactions of the Metallurgical Society of AIME, Vol. 242, March 1968, 512-523.

[20] O'Dwyer, J.J., "Theory of Dielectric Breakdown in Solids", Journal of the Electrochemical Society, Vol. 116, No. 2, February 1969, 239-241.

[21] Klein, N. "Electrical Breakdown in Thin Dielectric Films." Journal of the Electrochemical Society, Vol. 116, No. 7, July 1969, 963-972.

[22] Jonscher, A.K. "Electronic Conduction in Dielectric Films," pages 3-42 in Fredrick Vratny, Thin Film Dielectrics, Dielectrics and Insulation Div., Electrochemical Society, New York, 1969.

CHAPTER III - INSULATION PHYSICAL CONSTANTS AND COMPARISON WITH SILICON

1. Introduction

It is the purpose of this chapter to relate and compare the physical characteristics of the most often used insulating films for silicon in light of the very stringent electrical, mechanical and chemical requirements imposed by the reverse biased diode. The ultimate goal of this comparison is to determine the implicit or explicit effect of these characteristics on surface leakage. If, for example, high electric field causes breakdown or deterioration, the original conductivity changes. Similarly,great mechanical stress can bring about disruptions which can adversely effect leakage. It will be shown that the specific insulating material used over silicon has an effect on both electric field strength and mechanical stress. Similarly, other materials properties will be shown to affect ultimate device performance.

To implement this investigation, various data were gathered and compared in tabular form. These considerations led to the realization that further exploitation of some of these characteristics could extend the capabilities of processing semiconductor devices requiring passivating films and could lead to films improved from a reliability standpoint. This concept will be explored further in this chapter and in Chapter V.

A substantial portion of this chapter is devoted to comparative values of constants, such as dielectric constant, thermal coefficient of expansion or density. This proves to be useful in predicting stresses and in postulating mechanisms which could cause a change in performance which, in turn, could cause a shift in device performance to specified readings or a lowering of the life of the component.

A further purpose of this chapter will be to discuss the way in which device performance depends on physical effects in the insulating film only (as differentiated from relative physical constants).

2. Variability of "Physical Constants"

An inescapable consequence of any consideration of constants is the degree to which the constants are actually unchanging in value. This is important in any electrical material, but particularly important when the insulation participates in the situation electronics (as in insulated gate field effect devices), and when sizes are greatly miniaturized. Drifts with time are important, because such changes indicate alteration of the film. Variation in value with applied stress such as voltage or temperature occur, and the effect of such change should be considered if a very accurate prediction is to be made. For order of magnitude calculations, this is sometimes not necessary. Also of great consequence to reliability is that minute change that may occur as a result of changes in the method or conditions of film formation.

The import of very slight changes in one property in terms of properties of interest in electronic films can easily be deduced, although the specific internal change cannot. For example, a slight change in density could involve one or more of several mechanisms for which possible consequences in a device are listed:

Possible Change Mechanism	Consequence
1. Change in porosity	(a) Variation of electrical resistivity
and/or	(b) Modification of alkali ion migration
2. Change in short range structure	(c) Change in etch properties (hence affects processing)
	(d) Alteration of rate of acceptance of H_2O by the film. This may have further effects on film electrical properties.
3. Change in crystalline structure	(a) If large polycrystals exist, a drastic lowering of dielectric strength may occur.
	(b) Etch properties may be altered
	(c) Thermal conductivities may shift
4. Chemical reduction i.e., SiO in SiO_2, or Si in SiO	(a) Resistivity may be modified
	(b) Might cause shift of available surface states at layer of silicon.

5.	Chemical interaction at layer interface	(a)	Completely different compounds may be formed - $Al_2O_3 + SiO_2$ may form silaminite or mullite

Physical constants are usually not constant, as has been discussed above, but a listing of approximate room temperature values can serve a very constructive purpose.

This tabulation, Table IV-1, is supplemented by a bibliographical listing of the specific sources of information for this chart. With the exception of silicon, the table is divided for each substance to provide some comparison of the crystalline form of the material with the bulk and/or the film form. The bulk form of silicon dioxide is normally vitreous (glass), and the bulk form of silicon nitride or aluminum oxide is probably polycrystalline. In some instances more than one value is listed, with an appropriate reference. This may represent a true difference of values and consequently some change in the physical nature or chemical makeup of the sample. This is not totally unexpected when we consider that the processes by which samples were prepared were often different. On the other hand, small differences in values may result from differences in technique used by various scientists in measuring these constants. This investigator did not try to act as a referee in any of these differences, nor was there an attempt made to critically examine the exact techniques of measurement. This table is intended primarily to give comparisons of values, such as the coefficients of thermal expansion of vitreous silica vs. that of crystalline quartz. Even more important is the question as to whether or not the involved property of the protective layer varies markedly from silicon and some interest in whether the constant is numerically greater or less than the equivalent constant of silicon. In those instances for which an absolute figure is required (e.g. dielectric strength, resistivity, thermal conductivity or melting point) the agreement is sufficient for many practical reliability purposes.

The values shown for silicon in Table III-1 are for intrinsic or very pure, crystalline silicon. It is a well-known fact that certain impurities (donor or acceptor elements) can vitally change the resistivity. Other properties may also be expected to change with these impurities or "doping" concentrations, and in fact rather striking property changes with respect to light (infra red) absorption occur[1] but are not charted.

The term "amorphous" for purposes of this tabulation means primarily "no long-range structure." Polycrystalline form may well be involved, providing only that the constituent true crystals do not exceed, on the average, 50 Å in size. In the case of SiO_2 we can extend amorphous to also imply "vitreous" or "glassy" at least for those films processed a few hundred degrees away from the softening point of SiO_2. Whether the SiO_2 films formed by ion bombardment are truly glass by

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[1] Runyan, W.R., Silicon Semiconductor Technology. New York: McGraw-Hill, 1965, p. 195.

nature is not known, but it could be postulated on the basis that Zachariasen's rules for formation of a glass are satisfied by SiO_2 that the amorphous form could be glass. That this has a significance cannot now be demonstrated, but many phenomena which are connected with electronic behavior are intimately tied to structure such as binding forces, efficiency of packing, etc. Quartz and amorphous silica serve as an example of this. Ions will not migrate through quartz crystals, although a small ionic current occurs in one crystal direction if ions are replaced.[2] On the other hand, in amorphous silica, alkali ions migrate readily through the layers. The interaction of ion drift with electronic behavior of field effect devices is well known.

The electric field in the immediate vicinity of a p-n junction is usually very large when the junction is negatively biased. Typically, if the depletion region is .001" in extent and a potential of 1000 volts is applied across the junction, a field of 1000 volts/mil or approximately 400,000 volts/cm exists. Even some of the better bulk ceramics and almost all organic insulation materials fail under such a field strength. The few exceptions - for example a technique was developed by Brenneman and Gregov[3] for producing epoxy films with a breakdown

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[2] Private Communication with Dr. R.E. Doremus, General Electric Company.

[3] Brenneman, A.E. and Gregov, L.V., "Epoxy Dielectric Films Produced by Electron Bombardment," Journal of the Electrochemical Society, Vol. 112, 12, December 1965, pp 1194-1197.

strength of 10^6 v/cm - still have the disadvantage of the presence of carbon which is very likely to "track" a conducting path in the event of high leakage current. This same comment applies to silicone films.[4]

3. The Nature of the Silicon-Insulation Interface

One should be aware of the very sensitive nature of the surface with which one is dealing. Recapitulating from Chapter II: (1) Many energy levels exist between the valence and conduction bands at a silicon-vacuum surface due to the abrupt termination of the crystalline lattice such as the Tamm States. (2) These energy levels tend to degrade performance. (3) Most surface insulating coatings tend to diminish the number of energy levels between the valence and conduction bands. (4) Charge concentration in the insulating coating can induce mobile carriers (holes or electrons) to the surface which change conduction.

The "interface" between silicon and the protective film, whether it is silicon dioxide or silicon nitride, has a bonding which does not constitute a perfect match in terms of mechanical or electrical properties. For example, the coefficient of thermal expansion for silicon is 2.3×10^{-6} per degree

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[4] Conti, M. and Tegagni, F., "Electrical Properties of Silicone Films on Silicon." Journal of the Electrochemical Society, Vol. 116, No. 3, March 1969, pp 377-380.

C whereas that for amorphous silicon dioxide is 0.3×10^{-6} per degree C and for crystalline silicon dioxide 9×10^{-6} or 14×10^{-6} per degree C depending on the crystal direction. One can see that if this structure goes through temperature changes, stresses and strains are set up, and in the long range this mechanism has the capability of disrupting bonds. The maximum stress will occur at the interface, and it is logical to assume that the abrupt termination of the silicon crystal will bring about microscopic areas of bond weakness. It is conceivable that a cleavage between the two layers could start at such a point. Any such separation would in itself provide a lowering of dielectric strength along the cleavage, and would provide a path for moisture or other impurities to move relatively freely.

It will also be logical that electric fields of high magnitude could produce ionization of moisture or other gases that may be present and thus further increase the rate of deterioration.

4. The Table of Comparative Values

Table III-1 displays the physical properties of silicon monoxide, silicon dioxide, silicon nitride, and aluminum oxide along with silicon for comparative purposes. As has been previously stated, the numbers charted represent the value of the constant at room temperature unless otherwise noted, with no attempt to consider a functional relationship of charted values with temperature, mechanical stress, applied field, or with any other factors which could, and in practice bring about a change in the material properties of these layers.

5. Coefficient of Thermal Expansion

A brief earlier mention of relative thermal coefficients of expansion will be explored in a more quantitative manner. In grown SiO_2 surfaces on semiconductors; an amorphous oxide film is formed. Let us take an example of a .025 cm thick silicon wafer upon which the film thickness is 5000 Å. The temperature of formation is typically 1050°C. Hence, ΔT will be approximately 1000°C to cool the wafer to the temperature at which it will be used. It is assumed for simplicity of calculation as a first order of approximation that α (the temperature coefficient of expansion) is a constant.

Since the thickness of oxide is several orders of magnitude less than the thickness of silicon, the oxide may be considered to influence the total linear shrinking very little; hence, the elongation is taken to be 2.3×10^{-6} inches per inch of length per degree Centigrade change.

$$\Delta \text{ length} = 2.3 \times 10^{-6} \times 10^{3} \text{ [basis 1 inch]}$$

This represents total elongation of silicon plus layer, but in this calculation the layer only is considered below.

Of this change in length, the SiO_2 temperature shrinkage would have accounted for 0.3×10^{-6} inches per inch of length. Had only this amount of shrinkage occurred, there would be no net stress left in the film. It is assumed that stress is proportional to strain. Shrinkage above 0.3×10^{-6} inches per inch of length will produce a proportional compressive stress in the oxide layer.

$$\text{length, net} = 2.3 \times 10^{-3} - 0.3 \times 10^{-3}$$

$$\Delta = 2.0 \times 10^{-3} \text{ inches/inch}$$

(which must result in stress in the SiO_2)

$$\frac{\text{Stress}}{\text{Strain}} = \text{Young's Modulus}$$

$$\frac{\text{Stress}}{2.0 \times 10^{-3}} = 10.5 \times 10^{6}$$

$$\text{Stress} = 21 \times 10^{3} \text{ psi}$$

Hence, stress = 21,000 psi

R.J. Jaccodine and W.A. Schlegel[5] measured the actual stress under similar conditions to be 45,000 psi.

It is concluded that amorphous SiO_2 on silicon formed at high temperature and used at low temperature is satisfactory, but under considerable stress.

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[5] R.J. Jaccodine and W.A. Schlegel, "Measurement of Strains at Si-SiO_2 Interface, Journal of Applied Physics, Vol. 37, No. 6, May 1966, pp 2429-2434.

Crystalline silicon dioxide, on the other hand, differs greatly from silicon in its thermal coefficient expansion. Further, the net resulting insulating film would be in tension after cooling. Normally we would not expect to deposit crystalline SiO_2 but continued exposure of amorphous films to high temperature might cause devitrification, similar to fused quarts tubes after continued use in a refractory furnace.

Amorphous silicon nitride, with an α of 2.5×10^{-6}, should result in a low stress film, but under tension. Aluminum oxide should result in higher stress film under tension.

The idea of combining films of diferent composition to produce low stress is being explored by C.M. Drum and M.J. Rand[6]. An interesting possibility exists that if during coating the surface only were to be heated suddenly with pulses of energy. The end result would be a film with its own stress, but without the additional stress due to the silicon expanding and subsequently shrinking. This will be explored further in Chapter V.

6. Dielectric Constant and Dielectric Strength

The dielectric constants of silicon and the insulating layers effect device performance in various ways. First, consider the insulation over doped silicon in those regions of a

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[6] C.M. Drum and M.J. Rand, "A Low-Stress Insulating Film on Silicon by Chemical Vapor Deposition," Journal of Applied Physics, Vol. 39, No. 8, August 1968, pp 4458-4459.

wafer where the silicon is normally conductive. The dielectric constant of the insulator relative to that of silicon is unimportant. A very low dielectric constant of the insulator will reduce the capacitive coupling of the conducting silicon to any nearby deposited wiring, particularly if the wiring is very near the conducting silicon. A low dielectric constant will also reduce the field concentration above the dielectric for fields induced between the silicon and any conducting object above the layer. For this purpose, silicon dioxide $K = 3.7$ or silicon monoxide $K = 3+$ would be the best of the tabular values.

On the other hand, on the surface near the depletion region of a back biased junction, the underlying silicon is more of an insulator than a conductor and surface irregularities due to polishing or etching may permit the insulator to extend into the surface of the silicon. Etch pits are a common occurrence at surface dislocations. A deep polishing crack might not be removed by back etching. Any undisolved earlier coating would produce the opposite effect, that is a raised mesa or needle. In such a situation it is assumed that the sandwich effect of dielectric materials with differing dielectric constants will cause an intensification of the field in the material with the lower dielectric constant. This is a consequence of the continuity of the $\overline{D} = k\overline{E}$ vector across a boundary perpendicular to the field direction.

In silicon dioxide or silicon monoxide a pocket as described above could result in a threefold increase of the electric field, since k for silicon = 12 and k for SiO_2 = 3.7. The original field may be at a value of 4×10^5 volts/cm. (As developed earlier in this paper.) There is every indication that the basic dielectric strength will not be exceeded (tabular values indicate strength greater than 5×10^6 volts/cm) but the high field may cause ionization, ion migration, or other degrading phenomena. As an example of such other possibilities, consider quartz, which is in some forms piezoelectric. Added electrical stress could cause added mechanical stress which was earlier in this chapter shown to be very high.

To prevent such a field increase near a junction, a higher dielectric constant, k, would be desirable. Hence, for this purpose silicon nitride or aluminum oxide would be indicated. k for silicon is 12, for silicon nitride 10, and for aluminum oxide 10. The use of insulating layers with a dielectric constant higher than silicon could bring into play tantalum oxide k = 20 or titanium dioxide k = 100. [These materials are not charted.]

It should be noted that with a k higher than silicon, the combination would be susceptible to any spires of silicon extending into the insulating layer. This would cause field concentration in the silicon.

The dielectric strength of tantalum oxide (not tabulated) is known to be high. Insofar as reliability is concerned, tantalum oxide as utilized in electrolytic capacitors also enjoys a good reputation in military equipment. Titanium dioxide in relatively thick (0.1 inch film) has a dielectric strength in the neighborhood of 300,000 volts/inch.[7]

7. Resistivity

With the exception of silicon, the lowest value listed in the column of resistivities is silicon nitride with a ρ of 10^{12} (minimum). If we postulate a 5000 Å thick film over a linear junction frontage of, say, 0.5 mm., we obtain for a uniform field strength of 10^6 volts/cm a leakage of 2.5×10^{-12} amperes. Since even very sensitive signal diodes usually have leakages measured in nanoamps, resistivity is not a matter of concern in the protective layers. In the silicon itself, the resistivity is listed at 2.5×10^5 and under the same conditions of field, a current of several microamperes is calculated. Fortunately, under high field, the resistivity of silicon increases. (Runyon, p 172)

Resistivity through the layer may not account for the entire drop of voltage in the depletion region. In Chapter I another mechanism was postulated. The few thousand Angstrom units of depth of the film is by far a shorter distance of resistive path than the 2×10^{-3} to 3×10^{-3} cm along the top surface of the insulating film. If, however, the surface resis-

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[7] Englefield, Lolin G., Vivienne J. Harwood and L.W. Toso, "High Voltage Breakdown of Titania in Vacuo." IEEE Transactions on Electron Devices, Vol. ED-14, No. 8, August 1967, pp 443-449.

tivity is for any reason lowered, the share of voltage drop along the surface may be much less than the voltage drop through the film. This is an important case, since a very similar situation exists when the full voltage drop is across the film. This full voltage drop does occur across the insulating layer in the case of interconnecting wiring, and in this case, as well as the case postulated, even extremely high resistivities (i.e. $\rho = 10^{12}$) may allow leakages well above those of the reverse biased junction.

8. Influence of Moisture

Moisture has a profound effect on resistivity. A perfect seal to exclude all water from a package is still a goal for future electronic devices. Semiconductor devices are sealed in glass, encapsulating resin and metal cans. Water permeates most resins with time. Metal cans for semiconducting devices must have provision for insulating leads into the device, which normally are glass.

Water is absorbed in glass, with two mechanisms apparent. A. Jelli[8] points out this distinction. Below 150°C, the surface is involved, and the water is not dissociated. Above 300°C the adsorption is chemical and involves the bulk of the material. Since glass is manufactured and worked at temperature above

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[8] Jelli, A. "Physical and Chemical Adsorption of Water by Glass," Physics and Chemistry of Glasses, Vol. 8, No. 5, October 1967, Abstract #590, p 71A.

300°C, it is not unreasonable to expect that ordinary glass contains bulk moisture which can diffuse to the surface. The experience of R.P. Misra provides an example that he personally encountered with T.V. tubes.[9] In this instance water continued to diffuse from the glass tubes eventually causing a deterioration in the cathode ray tube barium oxide emitting surface. G.J. Copley in studies of sheet glass determined the gas came out in two stages. First the surface water, and then the diffused bulk water.[10] R.H. Doremus has determined that the quantity of water adsorbed is related to a free volume which is less than the free volume defined by the difference of the theoretical density and actual density of fused quartz. Doremus believes the bulk water is molecular in form (i.e. not ionized).

Point by point the elements are inferred: (1) If glass is used, water vapor will be present, unless extraordinary precautions are taken; (2) Water vapor will certainly be adsorbed in silicon dioxide, at first on the surface, then more slowly throughout its bulk; (3) Water vapor has an electrical effect on pure silicon. The effect of water on silicon terminated in an oxide layer may be less when we consider only the change in the number of surface states created by the presence of water;

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[9] Dr. Raj P. Misra, Lectures in Reliability Engineering, Newark College of Engineering.

[10] Copley, G.J. "Internal Friction Studies of the Dehydration of Sheet Glass." Physics and Chemistry of Glasses, Vol. 8, No. 1, February 1967, pp 38-44.

(4) Water, in general, makes surface conduction more favorable, particularly in the presence of any ionizable impurities. [This was demonstrated by Lewis and Bohrer(Ref. 4, Chapter I) at least for ceramic substrates.]; (5) It is conceivable that water makes better conducting paths through solid insulating films, but this is not necessary for our argument.

The mechanism justified by these conditions was described briefly in Chapter I. The leakage path is from "n" or "p" carrier semiconductor bulk through the thin film to the thin film surface, along the surface, then back through the thin film to the opposite carrier semiconductor bulk. There is nothing to prevent the extension of this mechanism to include the secondary covering material (perhaps epoxy) which is bonded to the upper surface of the primary protective layer (in this case probably silicon dioxide, silicon nitride or aluminum oxide). Since many resins have more or less affinity for water, the resistivity might be expected to be much less than 10^{12} ohm-cm, the minimum value of these insulators displayed in the tabulation, Table III-1.

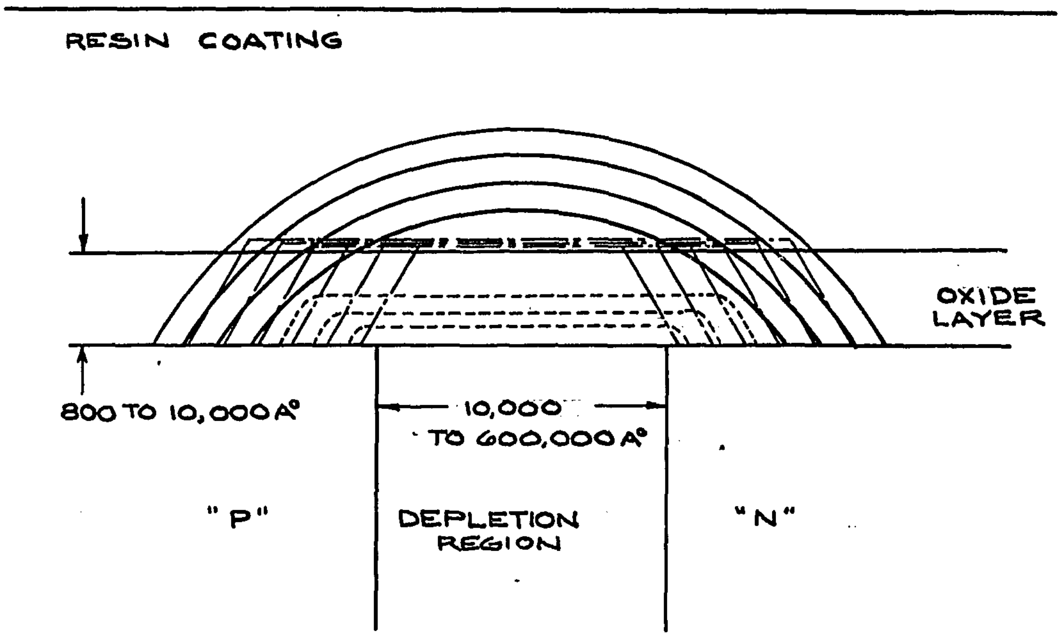
The conduction under these conditions will consist of the back biased bulk semiconductor junction flow in parallel with the series combination of the insulator surface flow and two thicknesses of insulation. Included in the insulator surface flow there may be three distinct types of flow: (a) flow inside the oxide (or nitride) layer only, (b) flow through the oxide, thence along the oxide-secondary insulation surface, and (c) flow through the oxide, then into and along the secondary insulation.

Flow along the surface just inside the silicon may occur if carriers are attracted by surface charge. Figure 1 illustrates these various flow paths. Each element of this flow acts differently. The back biased junction current Io or Ico is essentially a constant, but may be larger under certain conditions if an inversion layer has spread the effective junction area. The primary protective layer resistivity will likely have a complex current-voltage relationship as noted in Chapter II.

Since the primary protective layers may range in thickness from 1000 to 10,000 Å, whereas the depletion region width might vary from 10,000 Å to several hundred thousand angstrom units, it is easy to visualize a productive conduction mechanism involving the surface of the primary insulation or the bulk of the secondary insulation. In Chapter IV, at least on specific units, the secondary insulation is shown not a likely dominating factor.

9. Optical Index of Refraction; Electromagnetic Absorption Coefficient

The optical index of refraction of silicon is considerably higher than that of the insulating coatings. For Si, $n \approx 3.5$, whereas for SiO_2 $n = 1.46$ and also Al_2O_3 $n = 1.65$ and for



KEY: ------- PATH #1, INSIDE PASSIVATION LAYER.

—·— PATH #2, THROUGH OXIDE LAYER, ALONG OXIDE - RESIN INTERFACE, THEN BACK THROUGH OXIDE LAYER.

——— PATH #3, SIMILAR TO PATH #2, EXCEPT IT INCLUDES EXCURSION INTO RESIN ENCAPSULATION

NOT SHOWN: SILICON SURFACE CONDUCTION DUE TO ATTRACTION OF CARRIERS BY CHARGE TRAPPED AT SURFACE OR IN PASSIVATION LAYER

FIG III-1. FLOW PATHS THROUGH AND ALONG PROTECTIVE SURFACE OF SILICON AT A BACK BIASED JUNCTION.

Si_3N_4 n = 1.93. Under these circumstances, the silicon-insulator boundary will reflect a portion of the radiation.

In addition to the reflection due to difference in optical index of refraction, the electro-magnetic absorption coefficient of intrinsic silicon at 10.6 micron wavelengths is 1 cm^{-1} whereas for the insulating layers, the coefficient is in the neighborhood of 10^4 cm^{-1}. Hence, for a 10,000 Å film, the radiation will be absorbed primarily in the insulating film. The radiant energy will drop to 1/e of its initial value through the film. Then the film will gain even more energy because of the reflection discussed in the previous paragraph. This observation does not relate directly to film performance, but since a CO_2 laser can deliver very large power densities at a wavelength of 10.6 microns, this investigator believes that these characteristics will serve as an unusually good investigative tool, and perhaps be valuable in manufacturing processes.

At frequencies other than 10.6 microns, the ratio of absorption of energy in each layer is less. For example, in the range of wavelengths from one to three microns, both layers are relatively transparent. In the range of visible light, the silicon absorbs and the insulating film is relatively non-absorbing. It is within the realm of possibility that this last case might also be usable.

A sample calculation of differential heating by a laser beam will illustrate the capability of this technique. The calculation is made on a "worst case" basis, i.e. using the coefficient of heat conductivity of silicon, 0.34 cal/cm-sec °C, instead of that of silicon dioxide, .00457 cal/cm-sec °C. Since the thermal energy is released primarily in the silicon dioxide, the lower figure should dominate. As will be illustrated after the calculation, an increase in thermal radiant intensity will more than compensate for the rapidity of heat transfer in the silicon.

The following case is assumed: A silicon disc of thickness 0.03 cm is coated with a layer of silicon dioxide of thickness 10,000 Å. It is desired to calculate the effect on the silicon in the time it takes to evaporate the silicon dioxide from a spot 0.15 cm in diameter, using infra-red absorption from a focused 100 watt laser source.

The energy to heat the silicon dioxide to 1700°C is roughly:

$$E_{T_2-T_1} = \overset{\underline{\text{Area}}}{(.15)^2 \frac{\pi}{4}} \times \overset{\underline{\text{Thickness}}}{10{,}000 \times 10^{-8}} \times \overset{\underline{\text{Density}}}{2.6} \times \overset{\underline{\text{Sp. ht.}}}{.2}$$

$$\times \overset{\underline{\text{Joules/Cal}}}{4.18} \times \overset{\underline{\text{Degrees Rise}}}{(1700 - 100)} =$$

$$\approx 5 \times 10^{-3} \text{ Joules}$$

The latent heat of vaporization and fusion combined are estimated at 700 cal/gm.

$$E\ \text{evap} \approx \text{mass} \times 700 \times 4.18 = 13.6 \times 10^{-3} \text{ Joules}$$

$$E\ \text{Total} \approx 19 \times 10^{-3} \text{ Joules}$$

At a rate of 100 joules/second (laser beam), the energy is absorbed at a rate of 64 joules/second in the silicon dioxide, if we assume the coefficient of absorption is 10,000 cm^{-1} as is the case of silicon nitride or aluminum oxide.

The difference in the optical index of refraction, n, of air compared to silicon dioxide and the difference of n in silicon dioxide compared to silicon also affects the relative distribution of energies in the laser beam. At the initial air-SiO_2 interface, Fresnel's Formula:

$$I = \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2$$

shows about a 3% loss. This does not affect the relative heating, and it is assumed the beam contains slightly more energy than 100 watts to provide 100 watts entering the silicon dioxide.

Between the silicon dioxide and silicon, the calculation of reflection is

$$I_R = \left(\frac{3.5 - 1.46}{3.5 + 1.46}\right)^2 = .17 \text{ or } 17\%$$

Of the 34 watts <u>not</u> absorbed in the 10,000 Å of silicon dioxide, roughly only 30 watts will be available to penetrate the silicon.

The absorption in the silicon is:

$$\begin{aligned} E \text{ Absorbed} &= 30\ (1-e^{-(1)(\text{thickness})})\text{ joules/second} \\ &= 30\ (1-e^{-1(.03)}) \approx 1 \text{ J/sec.} \end{aligned}$$

Since the silicon is $\frac{.03}{10^{-4}} = 300$ times the thickness of SiO_2, and the heating rate 1/64th the heating rate of the silicon dioxide, the radiant heating rate per gram of material is about $\frac{1}{18{,}000}$ that of the SiO_2. This factor is negligible.

The total time involved for absorbing 19×10^{-3} joules in the silicon dioxide is $\frac{19 \times 10^{-3}}{64} \approx 3 \times 10^{-4}$ seconds.

The other factor to consider in the silicon is how much heat conducts during the time of evaporating the surface layer. For a very crude approximation, consider a temperature difference of 1600°C and a thickness about 1/2 the thickness of the silicon or .015 cm.

$$\frac{\Delta Q}{\Delta \text{time}} = \frac{\Delta T \times K \times \text{area}}{\text{thickness}} = \frac{1600 \times (.34)\ (4.18) \times 1.78 \times 10^{-2}}{.015 \text{ cm}}$$

$$= 2700 \text{ joules/second}$$

At this point, it appears impossible to reach the temperature of evaporation due to the competing mechanism of thermal conduction. The input energy is 64 joules/second and the loss is 2700 joules per second. However, as emphasized earlier, our assumed conditions were modest compared to available apparatus. For example, a good lens could concentrate a beam to one-tenth of the diameter assumed, providing a loss of $\frac{2700}{(10^2)}$ or 27 joules per second. Secondly, more powerful lasers are available, including 1KW industrial to 10 KW experimental. If that were not enough, which indeed it is, we might take a more realistic value of thermal conductivity, since the greatest amount of heat generation is in silicon dioxide which has a lower conductivity. Thus, we have three factors of about 100 each favoring the proposed evaporation of silicon dioxide. This should supply a factor of safety of about 10,000.

A more careful examination of the heat transfer balance is in order for a future calculation. It was not deemed necessary at this time because of the high margin of probable success noted above. Further, even with a crude, hand-ground lens an 80 watt laser beam was utilized by this investigator to directly sublime quartz into the atmosphere.

Returning to the original (worst case) calculation, the question arises as to the temperature the silicon will attain during the 3×10^{-4} seconds necessary to evaporate the silicon dioxide.

$$\Delta Q = 2700 \times 3 \times 10^{-4} = .71 \text{ joules}$$

$$= .17 \text{ calories}$$

with a mass of silicon of: $M_{si} = 1.78 \times 10^{-2} \times .03 \times 2.3$

$$= 1.25 \times 10^{-3}$$

$$\Delta T \times C_v \times 1.25 \times 10^{-3} = .17 \text{ calories}$$

$$\Delta T = \frac{.17}{.18 \times 1.25 \times 10^{-3}}$$

$$\Delta = 750° \; !$$

The same comments regarding improvement if the beam intensity is increased apply. If the rate were increased by a factor of ten by reducing the beam size, or increasing laser power, a ΔT of 75 centigrade degrees would ensue.

This technique which will be explored further in Chapter V serves as a particularly good example of interplay of physical characteristics, and comparative differences of the physical properties of two different materials. The wide divergence of infrared absorption characteristics permits selectively heating one layer. The diversity of optical index of refraction aids this cause by reflecting part of the energy at the interface of the two materials. The order of magnitude difference of thermal conductivity helps confine the heat to the silicon dioxide layer, but the very small thicknesses of the layers still permits a very great conductive heat flow in a very short time. The specific heat was utilized to determine temperature rises and, if the calculations had been continued to the point of determining stress in the silicon due to temperature gradient, the thermal coefficient of expansion, Young's modulus and strength would have been involved.

This same mode of heating might very well be utilized with a gaseous etch with much lower powers and no problems with the silicon.

10. Diffusion (Particularly Alkali Ions)

The ever present sodium ion, as well as most other monovalent ions have been found to diffuse rapidly in films of silicon dioxide. This has had a deleterious effect on MOS devices and could contribute to inversion layers or channels in conventional semiconductors. The description of inversion layers and ion migration has been covered in detail in Chapter II.

Silicon nitride has a diffusion coefficient for sodium 10 orders of magnitude lower than that of silicon dioxide. Considering the fact that the field-induced diffusion of sodium in oxide layers takes place in many seconds or several minutes, it is expected that the occurrence of troublesome quantities of sodium should not diffuse through silicon nitride until literally years of operation with voltage on. (One year is approximately 3×10^7 seconds.)

The silicon nitride resulting from a particular forming process, or the final silicon nitride after intermediate processes involving high temperature, does not invariably possess structureless perfection. Impurities in the reactants, variations in process, and even substrate conditions can affect the resulting film. That this change has a measureable effect on the physical character of the film is perhaps best illustrated by a diagram drawn by Dalton and Drobek, Figure III-2, measuring relative sodium distribution in oxide and nitride films (of various crystalline sizes) resulting from the diffusion of a surface concentration of radioactive sodium in these films for 22 hours at 600°C.

The results of interest are apparent from this figure.

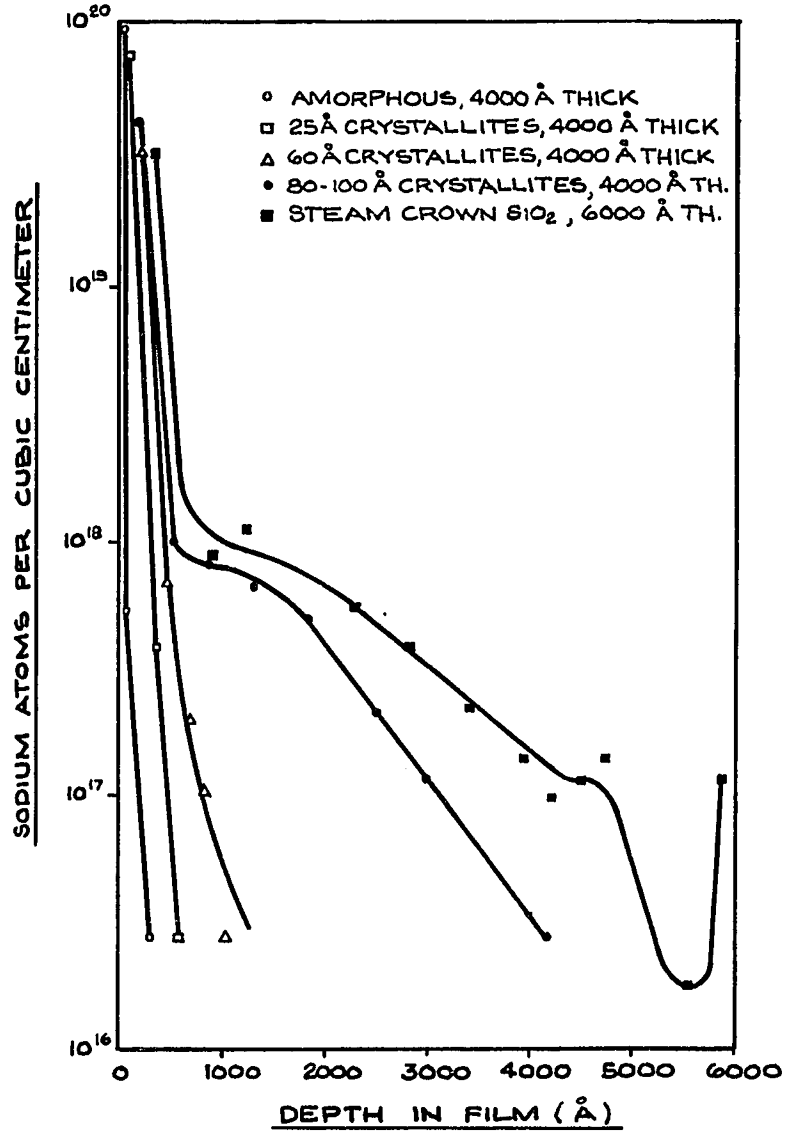


FIG. III - 2 SODIUM DIFFUSION PROFILES IN SILICON NITRIDE AND SILICON DIOXIDE

AFTER: DALTON AND DROBEK

Sodium diffuses much more rapidly in amorphous silicon dioxide than in amorphous silicon nitride. Secondly, the crystal size of polycrystalline material greatly affects the diffusion of sodium in silicon nitride. This is to be expected since the boundary surfaces between crystalline faces represent relatively weak binding forces with corresponding space for migratory ions. Dzimianski[11] discusses the significance of intercrystalline faces in passivating layers. He cites as a background example the diffusion of water along a crystal-crystal interface and its importance in corrosion technology.

Both of the above points are important. The most obvious conclusion is that from the standpoint of sodium diffusion, amorphous silicon nitride is by far the best material to use. In MIS films tested for ion flow induced by voltage, the tests show that this problem is indeed minimized with silicon nitride.

What cannot be shown in the chart of comparative properties of insulator and silicon is the dependence of the properties of a single type of film on the method and conditions of forming. Dalton and Drobek's diagram shows silicon nitride films of many crystallite structures, ranging from 100 Å to apparently amorphous films. In the accompanying article, Dalton and Drobek discuss the various methods they used for producing the films.

In Table III-1, the tabular values of dielectric constant

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[11] Dzimianski, J.W., E.R. Pemsel, W.J. Lytle, and S.M. Skinner. "Silicon Surface Passivation: Materials and Micro Properties," Physics of Failure in Electronics, Vol. 3, Rome Air Development Center.

show for silicon nitride in particular the disparity of physical constants with investigator and method. In Chapter II a very brief review of methods of film formation is outlined.

11. Structure

Most investigators have given values of density, dielectric constant, or index of refraction to provide comparative data to other films. What this information fails to convey is whether a lowering of these values is due to basic structural changes such as short-range packing, length of chains of molecules and eventual microcrystalline structure or due to porosity and defects in the layers. Electrically this could prove important. Porosity implies "inner surfaces" and this investigator would expect these inner surfaces to take up moisture and behave as a wet surface (i.e. poorly). A diagram of the electrical resistance of SiO_2 showing three orders of magnitude change with humidity is displayed by Grove and reproduced in Figure III-3.

Porosity may do more than supply a "surface" effect for inner adsorption of H_2O and other gases. The shape of the inner openings may contribute to abrupt boundary changes of field as covered earlier in conjunction with etch pits in silicon. The same reasoning would again apply. If a very high field is produced, even momentarily in a microspace with gases present, it is postulated that ionization occurs. This investigator did not attempt to measure or otherwise justify this

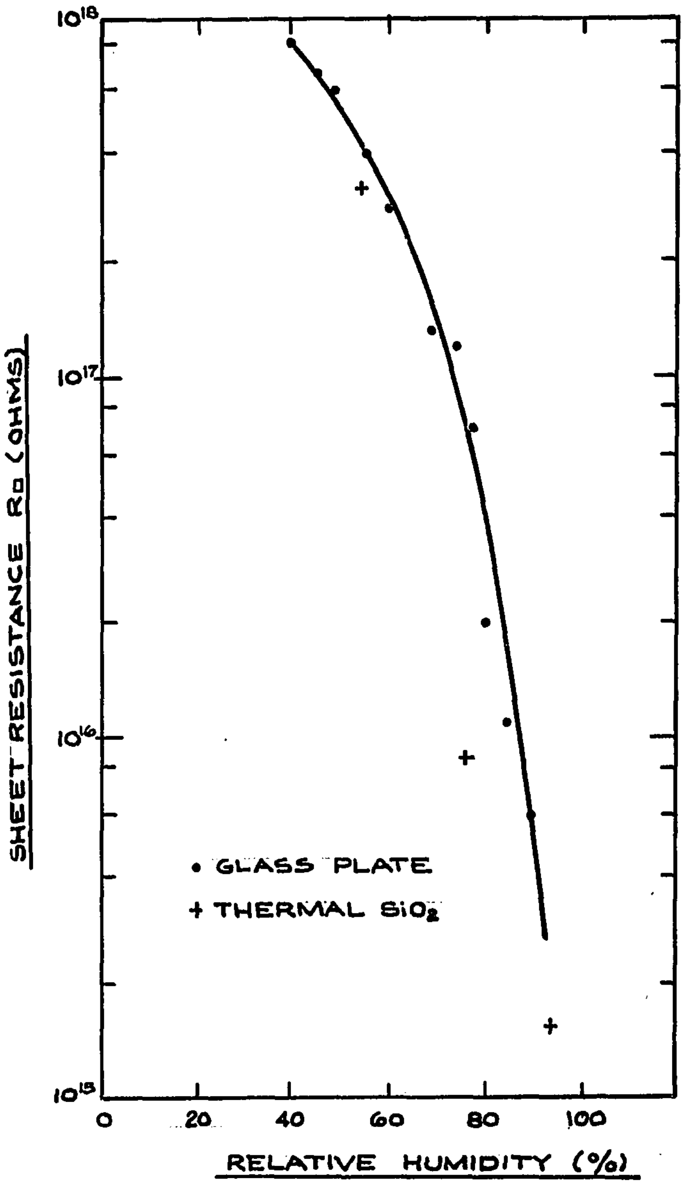

FIG. III- 3 SHEET RESISTANCE OF GLASS PLATE AND OF THERMAL SiO_2 vs RELATIVE HUMIDITY

AFTER: GROVE

hypothesis. Ionization, at the least, represents an energy of excitation, and this energy may be available for any chemical deterioration as applies to the particular situation. At worst, ionization could represent a momentary conducting path, reducing the effective depth of solid insulation. This, in effect, would be an exact reversal of the field concentration. Originally, the field would concentrate on the "cavity" which would then momentarily conduct through ionization. The total field would then be across the solid. Since the ion flow (for D.C. applied) would be temporary, the apparent bulk effect of many of these miniature pores would be that of polarization. Hence, polarization of a thin film may consist of the usual polarization of the dielectric (if it occurs), ion migration (if it occurs), trapping of carriers at the interface, and a polarization due to ionization in properly shaped pores.

Along a somewhat different line of thought, an ideal structure might be the utilization of an insulator that continues the crystalline pattern of the silicon. Hu has investigated this possibility for the case of crystalline silicon and crystalline α - Si_3N_4 with the conclusion that not all atomic spacings can be simultaneously matched.[12] In any event, the basic crystal spacings for the predominant crystal form are listed in the table of comparative values.

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[12] Hu, S.M. "Properties of Amorphous Silicon Nitride Films," Journal of the Electrochemical Society, Vol. 113, No. 7, July 1966, pp 693-698.

The subject of matching of properties can also include the possibilities of utilizing silicon as the insulating material. The physical match of doped silicon and intrinsic silicon could be virtually perfect. Theoretically it is possible to epitaxially deposit silicon, thus preserving crystalline structure. To date, however, such epitaxial deposits have been of relatively high conductivity. Future improvements may make such a structure practical. The tabulated value of dielectric strentgh, 4×10^5 volts/cm is more than adequate for most devices. The resistivity of single crystal silicon, 2.5×10^5 ohm-cm, is far too low, but this does not take into account the effect that field has in reducing carriers mobility and effectively raising this value at high field. Runyan shows this as about a tenfold effect.

The use of intrinsic crystalline silicon cannot easily be visualized as successful in an IGFET or similar device. The field attracting minority carriers to the interface of doped silicon-intrinsic silicon would enable these carriers to continue upward to the attracting electrode. This same effect would occur at the surface of a conventional transistor to some extent.

An electrically more attractive material might be amorphous silicon. Chittick, et al,[13] report preparation of

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[13] Chittick, R.D., J.H. Alexander, and H.F.Sterling. "The Preparation and Properties of Amorphous Silicon," Journal of the Electrochemical Society, Vol. 116, No. 1, January 1969, pp 77-81.

films with a resistivity of from 10^{10} to 2.5 x 10^{14} ohm-cm. If other physical properties were compatible with crystalline silicon, a successful device could result. It is possible this material could be used with an insulated gate device.

TABLE III-1 (6 Pages Following)

Tabulation of physical constants of Silicon, Silicon Monoxide, Silicon Dioxide, Silicon Nitride, and Aluminum Oxide.

The sources for these values are contained in references 14 through 54 at the end of this chapter.

		Crystal System	Lattice Constant	Hardness Moh
Silicon Si	Single Crystal	Diamond Lattice	(Interatomic separation ⑰ 2.34 Å 5.430 Å cube edge ⑱	7 ⑯
	Amorphous Thin Film	---		7
	Crystal (possibly exists)		7.09 Å	
Silicon Dioxide SiO_2	Amorphous Thin Film, Vitreous Silica	---		5 - 7 ⑳
	Crystalline: α Quartz (Other forms: β-Quartz, Tridimite, Ceosite)	Hexagonal	a = 4.9 Å c = 5.4 ㉜	
Silicon Nitride Si_3N_4	Amorphous	---		
	Crystal	Hexagonal	a = 7.7 c = 5.6 ㉑	> 9 ⑯
Aluminum Oxide Al_2O_3	Amorphous	---	a = 4.76 c = 14.00 ㊾	
	Crystal	Hexagonal		9 ⑯

		Dielectric Constant k or ϵ_r	Dielectric Strength E volts/cm	Resistivity Ω - cm
Silicon Si	Single Crystal	12 ⑰ 11.7 ㉑	4×10^5 for avalanche ⑱	2.5×10^5 ⑱ Thin film Amorphous: 10^{10} to 2.5×10^{14} (54)
Silicon Monoxide SiO	Amorphous Thin Film	3 to 6 ㉒ (increases with thickness)	3×10^6 ㉒	4×10^{12} ㉒
	Crystal (possibly exists)			
Silicon Dioxide SiO_2	Amorphous Thin Film, Vitreous Silica	3.7 ⑯	$>5 \times 10^6$ (56) (thin film) 10^5 bulk SiO_2 ㉛	10^{16} (thin film) (56) 10^{19} (vitreous)
	Crystalline: α Quartz (Other forms: β-Quartz, Tridimite, Ceosite)	4.4 (⊥ to axis) ㉝	$>5.5 \times 10^6$ ㊿	10^{14} ㉝
Silicon Nitride Si_3N_4	Amorphous	10 ㊱ 7 ㊴ 6.2-6.8 ㉕ 4.5-5.8 (51)	5×10^6 ㊳ 10^7 ㉞	10^{12} ㉑
	Crystal			Surface Resistivity 10^5-10^7 ohm/square ㉕
Aluminum Oxide Al_2O_3	Amorphous	8.81 bulk (55)	9.8×10^4 bulk ㉛	10^{14} bulk (55)
	Crystal	8.6 to 10/6 ㉛		10^{16}

		Thermal Coefficient of Expansion	Thermal Conductivity cal/cm-sec°C	Specific Heat cal/gm/°C
Silicon Si	Single Crystal	2.33×10^{-6} at 300°K ⑲	0.072 - 0.34 ⑱	0.18 ⑲ 0.168 ㊸
Silicon Monoxide SiO	Amorphous Thin Film			
	Crystal (Possibly exists)			
Silicon Dioxide SiO_2	Amorphous Thin Film	0.3×10^{-6} ㉛	0.00457 at 100°C ㉝	0.176 ㉗ 0.22 ㊸
	Vitreous Silica	0.5×10^{-6} ㊱	0.0049 at 100°C ⑮	
	Crystalline: α Quartz (Other forms: β-Quartz, Tridimite, Ceosite)	(9 to 14) x 10^{-6} ㉛ (8 to 13) x 10^{-6} ㊻	0.013 to 0.0215 ㉝ 0.013 0.023 ㊻	0.188 ㊸
Silicon Nitride Si_3N_4	Amorphous	2.5×10^{-6} ㊱	0.028 ㊼	0.23
	Crystal			
Aluminum Oxide Al_2O_3	Amorphous	9×10^{-6} ㉛	.078 (polycrystalline) ⑯ .103 ⑯	0.185 ㉗
	Crystal	8×10^{-6} ㉛		0.18 ㊸

		Young's Modulus, E psi	Strength psi	Diffusion Coefficient for Sodium, $cm^2/sec.$
Silicon Si	Single Crystal	23×10^6 ⑰	1.7×10^6 max ⑰	
Silicon Monoxide SiO	Amorphous Thin Film			
	Crystal (possibly exists)			
Silicon Dioxide SiO_2	Amorphous Thin Film Vitreous Silica	10.5×10^6 ㊹	2.0×10^4 (9th ed.) ㉟	1.6×10^{-9} at 400°C (52)
	Crystalline: α Quartz (Other forms: β-Quartz, Tridimite, Ceosite)	11.6×10^6 ㊺		
Silicon Nitride Si_3N_4	Amorphous	22×10^6 ㊽	7.7×10^4 ㊼	2.45×10^{-19} at 400°C (53)
	Crystal			
Aluminum Oxide Al_2O_3	Amorphous	53×10^6 ㊹	4.0×10^5 ⑯	
	Crystal	55×10^6 ㊹	2.2×10^6 max (whisker) ⑰	

		Optical Index of Refraction		Density	Melting Point °C
Silicon Si	Single Crystal	For λ = 1-10 in microns ⑲	index n 3.5-3.4	2.3 ⑰ 2.329 ⑱	1420° ⑰
Silicon Monoxide SiO	Amorphous Thin Film	at Na_n line	2.0	2.15 ㊶	Probably about 1700° ㊶
	Crystal (possibly exists)				
Silicon Dioxide SiO_2	Amorphous Thin Film Vitreous Silica	1.43 - 1.46 ㉚ ⑰ ㉗		2.649 ㉝	1710° ㉛
	Crystalline α Quartz (Other forms: β-Quartz, Tridimite, Ceosite)	1.54 ㉟			
Silicon Nitride Si_3N_4	Amorphous	1.93 at 6000 Å ㊲ 1.98 to 2.05 ㉞ 1.95 (51)		3.44 ㊱ 2.96 ㊴ 3.18 ㉑	Decomposes at about 1900° ㊵
	Crystal				
Aluminum Oxide Al_2O_3	Amorphous	1.59 - 1.65 ㉚		2.9-3.1 ㉚	2050° ㊷
	Crystal	1.76 to 1.765 ㉚		3.97 ㉚	

		Infrared Absorption Coefficient at λ= 10.5μ; α (cm^{-1})	Chemical Resistance
Silicon Si	Single Crystal	1 (Higher for "n" or "p" silicon) ⑲	Can be vapor etched by HCl, Cl_2, Br at high temperature. ⑲ Attached by 5% NaOH (boiling) ⑲ Attacked by HF and HNO_3 ㊵ Insoluble in HF ㊶
Silicon Monoxide SiO	Amorphous Thin Film	2.3 x 10^4 ㉓	Soluble in HF ㊶
	Crystal (possibly exists)		
Silicon Dioxide SiO_2	Amorphous Thin Film Vitreous Silica	$\gg$20 ㉔ (rough estimate 10^4)	Resistant to all acids except HF and hot phosphoric acid. Attacked by caustics. ㊵
	Crystalline α Quartz (Other forms: β-Quartz, Tridimite, Ceosite)		
Silicon Nitride Si_3N_4	Amorphous	7 x 10^4 ㉕	Very intert chemically, resists acids, caustics ㉑
	Crystal		Crystalline Si_3N_4 even more inert.
Aluminum Oxide Al_2O_3	Amorphous	(At 15 μ 2.5 x 10^4 ㉖	Very slightly soluble in acids and alkali

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CHAPTER IV

TESTING OF COMMERCIAL UNITS

1. Purpose

The theoretical and empirical formulations in Chapter II and the development of physical constants in Chapter III provide insight on the model of a practical semiconductor surface. In the region of a depletion layer caused by a back biased silicon junction, a passivating layer protects the surface from contamination, and at once lowers the number of surface energy states. The interplay of conductivity with changing very large fields, the change of surface condition with ion migration and the effect of moisture on surface conductivity all act to detract from the perfection of a practical device. Other factors covered in earlier chapters likewise influence the final behavior.

A major goal of this chapter is further quantization of the mechanism of leakage, particularly in those commercial units which show orders of magnitude increase in leakage under a humid environment. By test or construction from physical data, the relative contributions of current in completing leakage paths will be deduced. A further objective of this chapter is the comparison of the packaging and passivation combinations used in the various units tested insofar as the change in reverse current leakage.

2. SCRs as Diodes

A series of tests have been in progress over 7000 hours on several types of silicon controlled rectifiers (SCR). These tests were run in the reliability laboratory at NCE under conditions observed by this investigator.

The SCR units were stored under conditions which were designed to accelerate the failure mechanisms that are characterized by the Arrhenius rate equation or the Eyring rate equation described in Chapter II. It is recognized that there are ways in which temperature can inhibit failure (earlier examples have been given) and this situation is possible for a unit encapsulated in plastic. If the encapsulating plastic is not completely cured, there is a possibility that elevated temperature will help to complete that cure with a consequent improving of the electrical characteristics and a decrease in the permeability. Actually, completion of the cure may tie up catalyst or hardener molecules which would conceivably contain ionizable material. Some additional comment will be made further along in this chapter regarding the possibility that the application of humidity could affect the performance deterioration in an unexpected direction.

Three models of silicon controlled rectifiers hereafter designated as type T, type M and type G[1] were produced by three different manufacturers. Types T and M were oxide passivated, with a protective epoxy encapsulating package. Type G was oxide passivated with a silicone based resin package. No data as to the exact formulation of resin or filler was furnished by the manufacturers, since this is proprietary information. Figure IV-1 is a photograph of one of these three types of units. It is deliberately not identified as type T, M or G to prevent the possible identification of a given manufacturer with specific data.

These units are not identical units insofar as design is concerned. For example, one unit has a design forward current several times that of another. For this reason, the units will be compared with their own initial readings, and only the relative magnitude of the change shall be compared.

There may be complex ways in which surfaces have some influence in the mechanism of the relative injection efficiencies. This is not a prime consideration of this dissertation. On the other hand, some data are presented which are representative of these units as SCR's. The purpose of these data is to show that whatever change occurs has not modified the triggering voltage. This investigator postulated that this serves as evidence that bulk properties of the

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[1] Army Contract #DAAA-21-68-0-0500 - Progress Reports 1 thru 12. The designation M, T and G units is using the designation used in this report.

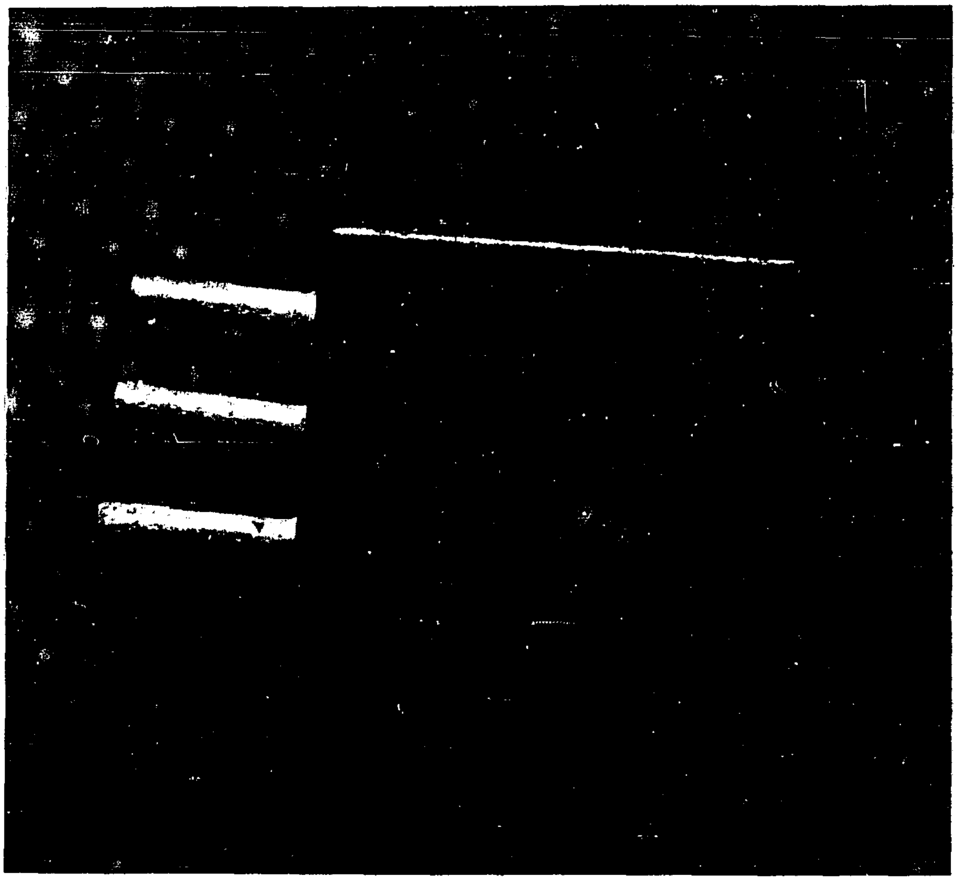

Figure IV-1. Plastic Molded Silicon Controlled Rectifier. This unit was used in temperature-humidity tests. Magnification approximately 10x silicon are not altered greatly during accelerated life testing.

An SCR with no gate voltage applied and a low forward voltage supplied acts very much as a reverse-biased diode. There are three junctions in an SCR and two of them are forward biased when positive voltage exists between the anode and cathode.

If the forward voltage gets too high, the injection efficiencies of the holes through the upper "n" region and the electrons through the lower "p" region may increase to the point that the unit fires. At very low forward voltage (say only a few millivolts), the forward biased junctions will contribute materially to the resistive path. An examination of the diode equation helps to visualize what probably happens.

While it cannot properly be assumed that all three junctions are identical, the purpose for which we use the diode equation is to show that the voltages across the forward biased diodes are only a small fraction of the total voltage. If I_o of the reverse biased diode were 20 times that of the I_o of the forward diodes, particularly the gate diode, no great difference in this conclusion would result.

The diode equation is:

$$I = I_o \left(e^{\frac{eV}{kT}} - 1\right)$$

and $kT \approx .026$ electron volts at room temperatures

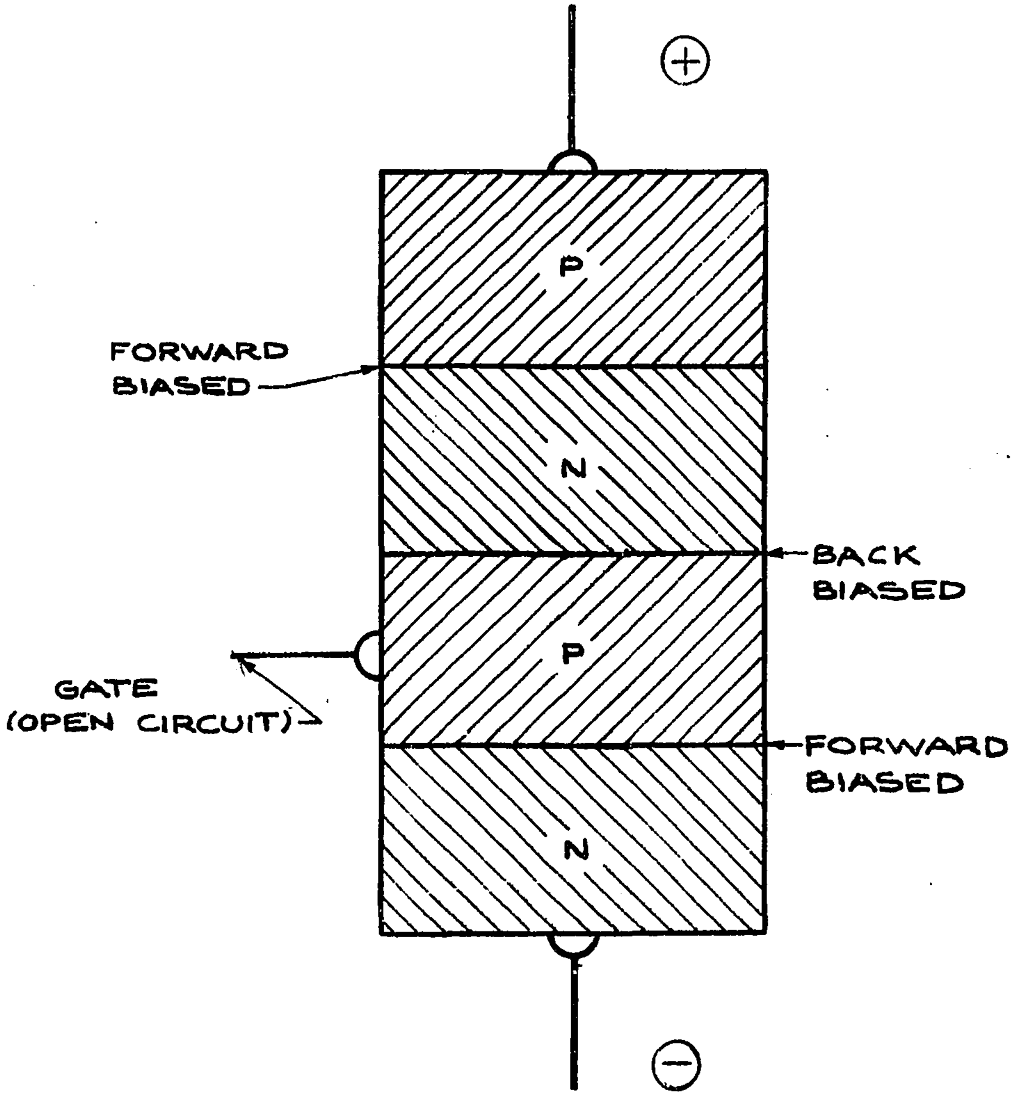

FIG IV-2 FORWARD LEAKAGE IN A SILICON CONTROLLED RECTIFIER at very low forward voltages

$$I \approx I_o \left(1 + \frac{eV}{kT} + \left(\frac{eV}{kT}\right)^2 \frac{1}{2!} + \ldots - 1\right)$$

If V is somewhat less than 0.026 volts, the solution for I will be a forward current of I_o. On the other hand, if V is negative, and rather large, $I \approx -I_o$. Hence, if the entire device has an applied voltage of 1 to 3 volts, I_o will be flowing, and the reverse biased junction will carry most of the applied voltage. To verify this theory for a very small diode, a signal diode was tested under conditions of very low applied voltage and the forward diode equation exponential effect is evident in Figure IV-3. A reading of 30 nano amps for an applied voltage of 0.020 volts (Figure IV-3) shows a considerably larger current than the measured leakage of the SCR units tested prior to temperature-humidity. This supports the earlier conclusion that of the 4 volts applied to these units, essentially all of it can be considered to be applied to the reverse biased junction.

3. SCR Accelerated Life Tests

Several measurements were made on these SCR's. The one used by this investigator is the reverse current leakage at 80% of the breakdown voltage. Readings were taken initially, then after each 250 hours of accelerated testing up to 1000

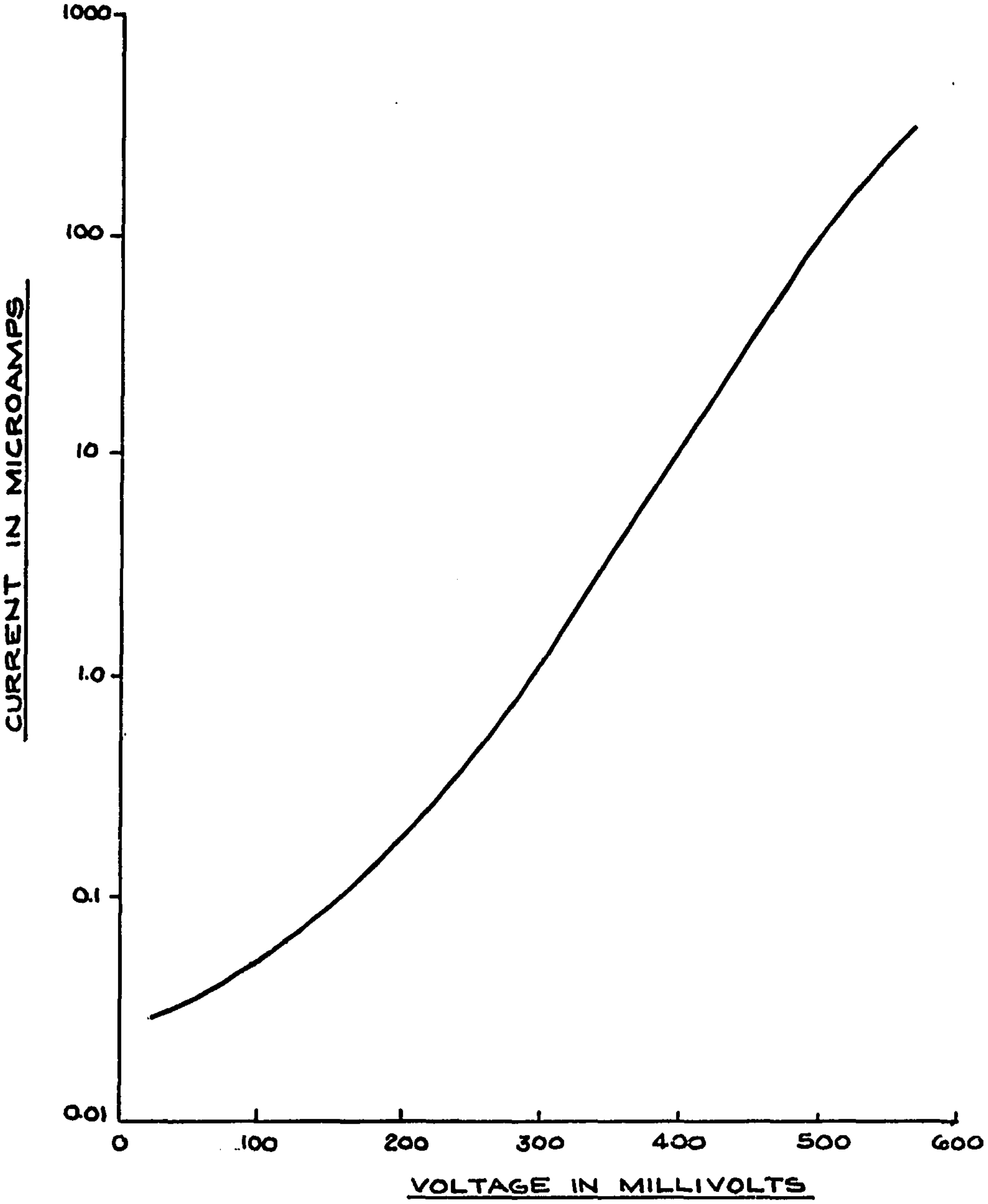

FIG IV-3 FORWARD CURRENT vs. VOLTAGE FOR A MICRO MINIATURE SIGNAL DIODE hours, at 1500 and 2000 hours and, thereafter, each 1000 hours. The environment was 95% R.H. at 65°C.

The relative current values for type A units increased drastically over the first 250 hours. Chart IV-1 is a bar graph of the average values of the leakage current. The initial value is consistent with an I_o of a typical silicon device. Chart IV-2 is a plot of the standard deviation of leakage current, and Chart IV-3 is a plot of the gate trigger voltage. The uniformity of this latter plot on linear scale is the key to the belief that leakage degradation is due to a surface mechanism. The exact nature of any such surface mechanism is very difficult to pinpoint. Some attempts to correlate the change with physical properties of the encapsulant is certainly a worthwhile task.

As an example of the behavior of the conductivity of a laminated plastic, which cannot be taken as totally representative of the case or molded resin in the test units, a figure is reproduced from Mathes[2] report on polymers which shows the change in volume and surface resistivity of a paper base phenolic resin after aging at 96% relative humidity.

Comparing this aging curve to Figure IV-3 which shows the change in leakage of type A units, the following striking similarities are apparent.

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[2] Mathes, K.N., "Electrical Properties of Polymers," General Electric Research and Development Center, General Chemistry Laboratory, Schenectady, New York, Report Number 67-C-257, June 1957.

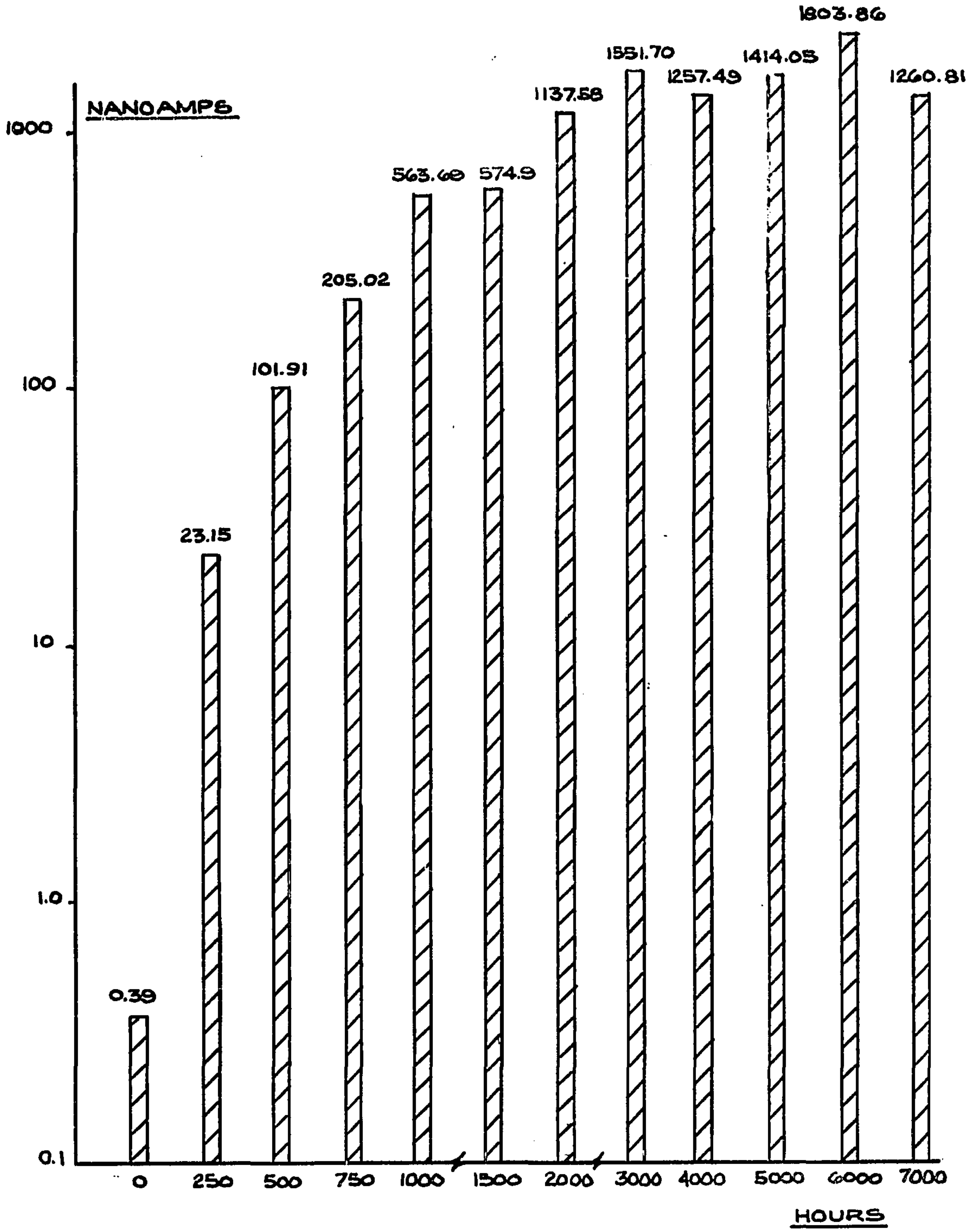


CHART IV-1 AVERAGE VALUE OF LEAKAGE CURRENT - TYPE "T" SCR

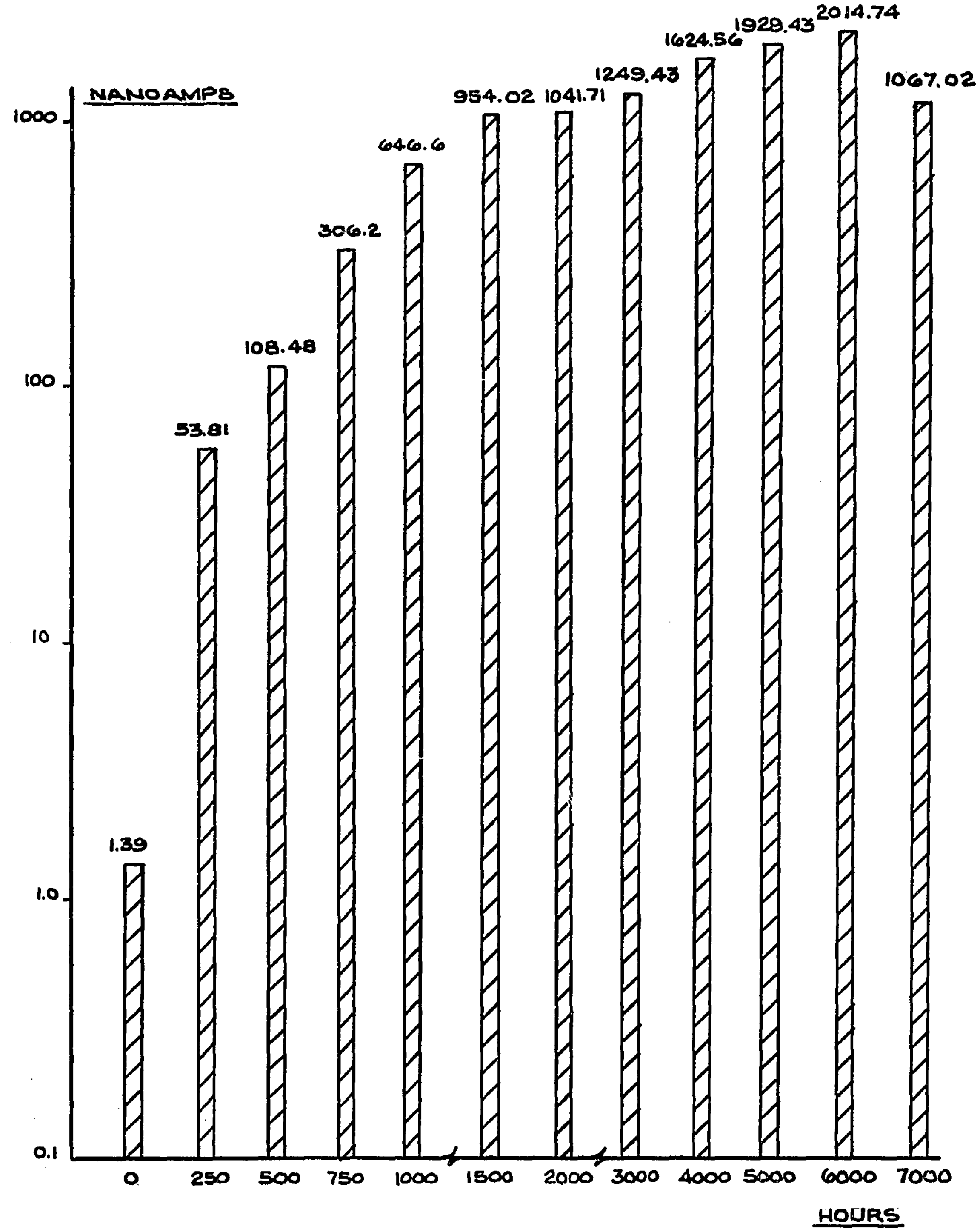


CHART IV-2 STANDARD DEVIATION OF LEAKAGE CURRENT - TYPE "T" SCR

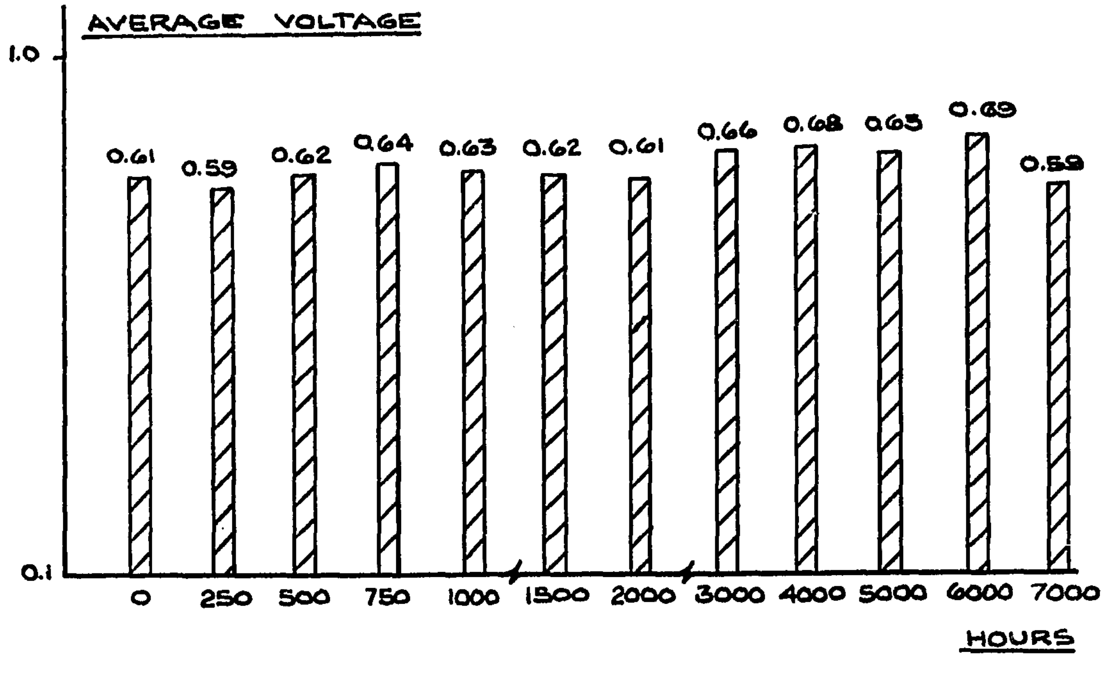
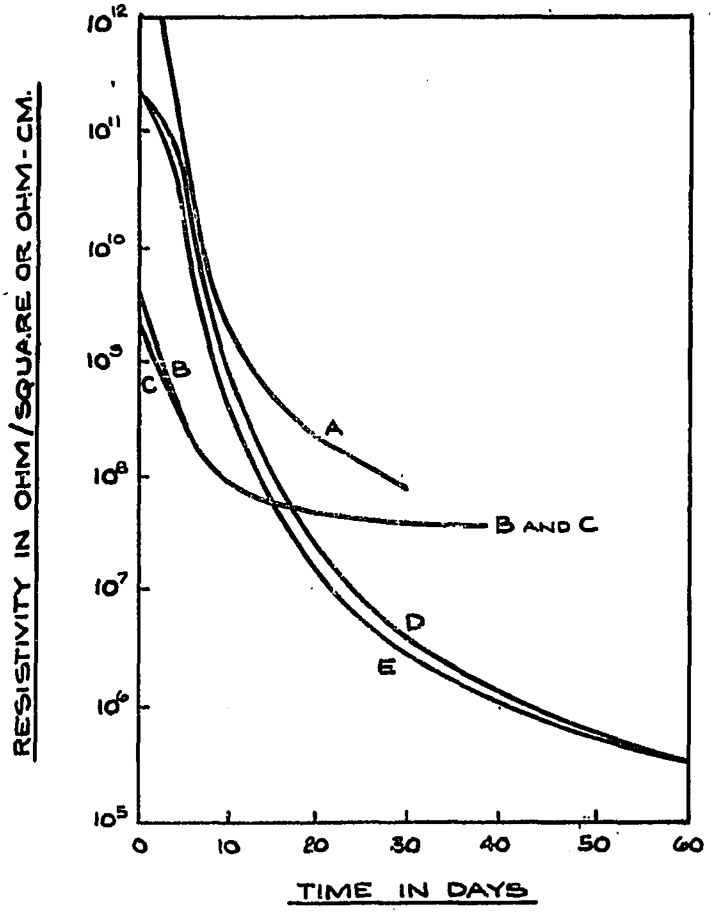


CHART IV-3 AVERAGE VOLTAGE OF GATE TRIGGER VOLTAGE - TYPE "T" SCR



KEY: A- VOLUME RESISTIVITY PERPENDICULAR TO THE LAMINATIONS.
B- SURFACE RESISTIVITY IN MACHINE DIRECTION.
C- SURFACE RESISTIVITY ACROSS MACHINE DIRECTION.
D- VOLUME RESISTIVITY ALONG LAMINATIONS IN MACHINE DIRECTION.
E- VOLUME RESISTIVITY ALONG LAMINATIONS AGAINST MACHINE DIRECTION.

FIG IV-4 CHANGE OF VOLUME AND SURFACE RESISTIVITY OF A PAPER-PHENOLIC RESIN LAMINATE ON AGING AT 96% rh AND 23° C. AFTER: MATHES

During the first 500 hours, the leakage of type A units increases by a factor of 400. During the first 20 days, the volume resistivity of the particular laminates studied decreases by a factor of 10,000. After 1500 hours, the "A" units average current changes very little. Similarly, after 60 days, the volume resistivity of the laminate changes at a much slower rate.

If the plastic leakage is to be equated to a possible cause of the diode leakage, then a mechanism must be postulated whereby an added three magnitudes of reverse current can flow in the diode-plastic combination. In Chapter III, attention was devoted to describing the current path through the passivating layer, along the surface, and then back through the passivating layer to the opposite carrier region of semiconductor. Under conditions of low surface resistance, it was deduced that a marginal voltage breakdown condition existed, with considerably increased leakage. The situation with the encapsulating plastic is not too different. In this case the leakage might again be surface leakage, or more properly, interface leakage between the plastic and the oxide coating. If such were the case, the previously postulated mechanism could account for the observed increase in leakage. The plastic serves as a protective shield when first placed in humidity, and then later, a saturation approaches, as a source of moisture to activate the interface mechanism.

To test whether the plastic itself provides a leakage path such a path is assumed, and probable flow lines are shown in Figure IV-5.

It is also necessary to have an estimate of the resistivity, ρ , of the epoxy resin after exposure to humidity. Measurements were made between leads on 25 units from which the active part of the SCR had been removed by grinding. These readings are tabulated in the appendix to this dissertation. The greatest leakage that occurred was 2.6 nano amps for an applied voltage of 4 volts. See Figure IV-6; Chart IV-4.

The resistivity was calculated using Smythe 4.13[5] (assuming two-dimensional flow):

$$R = 2\,\rho\,\cosh^{-1}\left(\frac{D^2 - R_1{}^2 - R_2{}^2}{2\,R_1\,R_2}\right)$$

where R = resistance measured, $\left(\frac{4}{2.6 \times 10^{-9}}\right) \times (.32)$

(the .32 cm to convert to resistance/unit depth)

D = distance between centers of leads

$R_1 = R_2$ = radius of leads

ρ = resistivity of material

D = .046 in.

$R_1 = R_2 = .010$ in.

$\rho \approx 1.02 \times 10^9$ ohm-cm

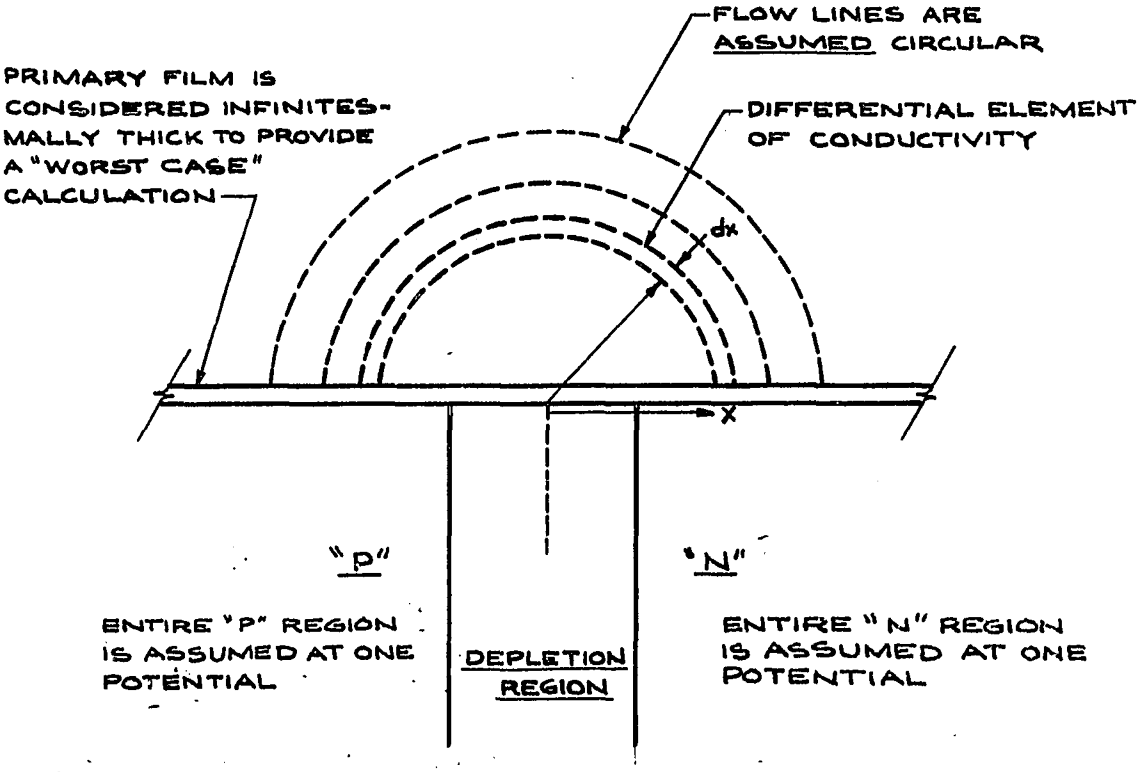
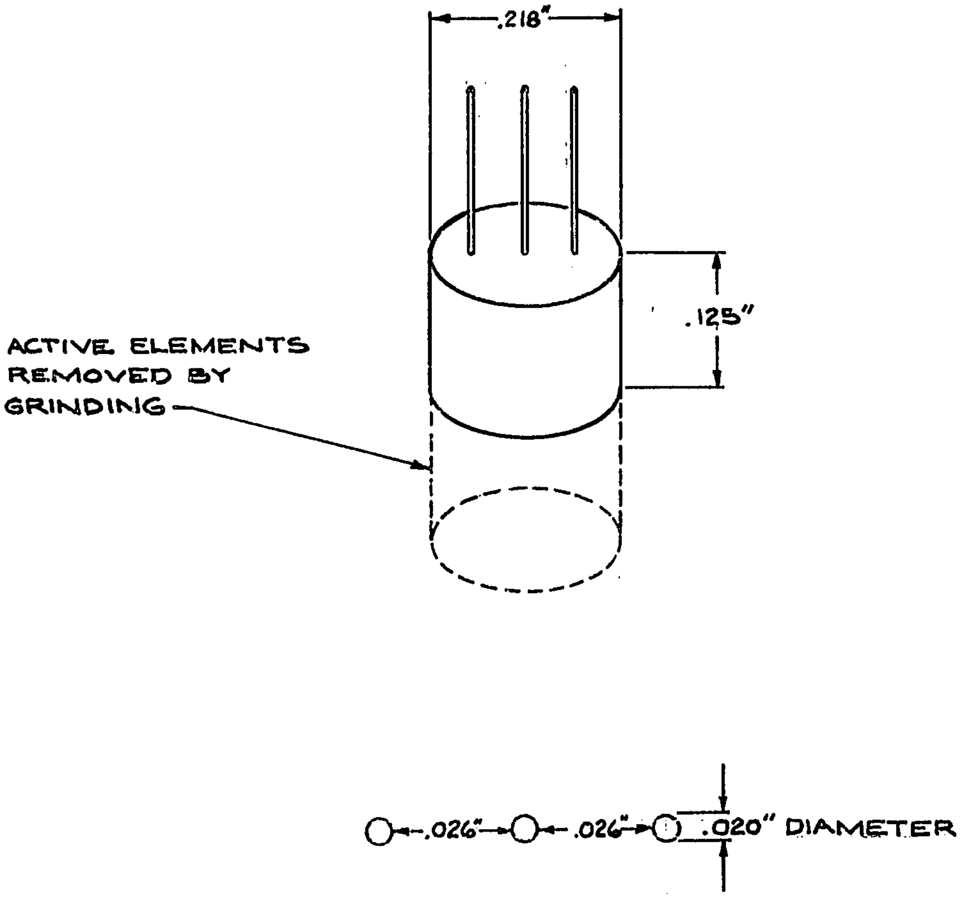


FIG. IV-5 ASSUMED FLOW THROUGH THE RESIN IN A PLASTIC ENCAPSULATED SCR UNIT



LEAD SPACING

FIG IV-6 SCR UNIT, WITH ALL ACTIVE ELEMENTS REMOVED BY GRINDING.

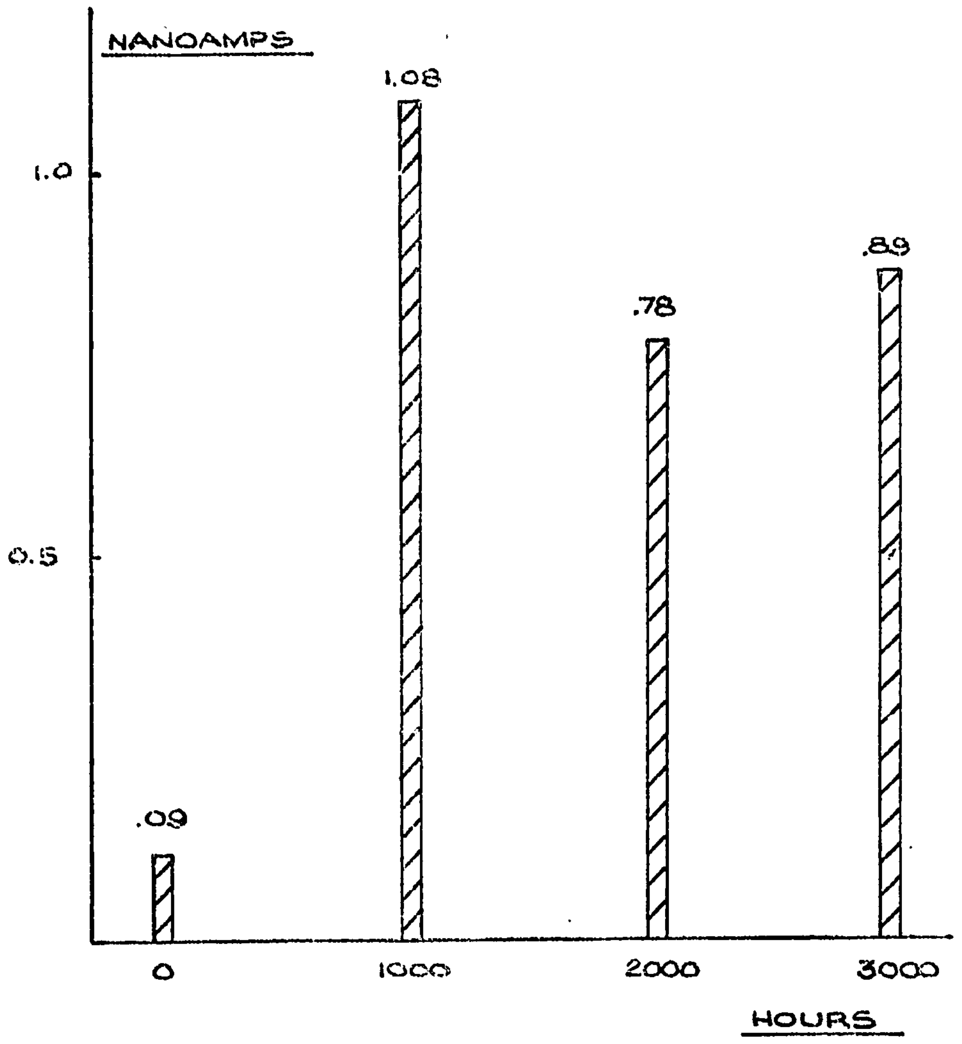


CHART IV-4 AVERAGE LEAKAGE CURRENT VS. TIME (IN HUMIDITY) - 25 SCR EPOXY LEAD-IN UNITS

(FOR DATA, SEE APPENDIX II-6)

Using an enlarged silver painted replica of the lead spacing on Teledeltos paper, a resistivity was measured to be $\rho = 1.2 \times 10^9\ \Omega$-cm. The smaller value $\rho = 1.02 \times 10^9$ was used subsequently since this would provide a more conservative value.

The contribution of the leads was measured and the current was 2.6 nano amperes. Using the established resistivity, $\rho = 1.02 \times 10^9$, a simulation and calculation is now made for the leakage in the resin across the depletion region. A typical value of 1.6×10^{-4} cm for the depletion width provides an approximate path length for the current flow through the resin as shown in Figure IV-5. By again simulating this condition with Teledeltos paper, a value of approximately 2 nano amperes was obtained. Experimentally, the dimensions of the deplection layer, the "n" and the "p" regions could not be established exactly.

A crude check, assuming circular flow lines, allows a simple calculation of the current flow. For convenience, the depletion region has been straightened out and can be visualized going into the paper. If the variable of integration is x, the resistivity is 1.02×10^9 cm, and the depth, t, is 0.3 cm, the conductivity is (taking the upper limit as 1 for convenience):

$$\frac{1}{R} = \frac{1}{\rho}\int_{x}^{1} \frac{t\,dx}{\pi x}$$

$$\frac{1}{R} = \frac{t}{\pi\rho} \ln x \Big|_{x}^{1}$$

Solving, $R = 1.2 \times 10^9$ ohms

Four volts would result in only a few nano-amps of current. Even if the estimate of the depletion layer thickness is in error by a large factor, the logarithm would minimize the current calculated through the plastic to a few times that originally calculated. It is difficult to visualize 1000 times this current flowing by this technique, unless the resistivity of the plastic varies considerably, and just happens to be 10^6 ohm-cm locally at the junction. This investigator does not believe that this is the case in these units. Measurements in glass passivated units, discussed later in this chapter, show similar leakage without the presence of the encapsulating resin. On the other hand, Mathes[2], page 18, states that small amounts of impurity in a polymer, such as catalyst fragments can cause an appreciable lowering of resistance. It is not beyond question that the droplets or particles of catalyst could be as large as the assumed depletion width, 1.6×10^{-4} cm.

The resistivity _vs_. time curves of plastic subjected to humidity shown in Figure IV-4 show change for a phenolic resin, but the question remains as to how closely epoxy case or molded resins might follow the humidity resistance _vs_. time curves. Possible evidence in this situation is obtained from a table prepared by Harper[3]. Two values of the volume resistivity for

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[3] Harper, Charles A., _Electronic Packaging with Resins_, McGraw-Hill, 1961, p 71.

epoxidized polyolefin are listed: At room temperature, the initial reading is 2.84×10^{15} ohm cm and after 7 days at 95% RH, at 60°C, the reading is 6.48×10^{13}. A quick comparison will show that the laminate curve drops approximately this extent in 7 days. Perhaps more important is the fact that the temperature-humidity conditions cited for this resin almost exactly approximate the accelerated conditions under which the SCR's were tested.

To some extent, the case at point is not conclusive because of incomplete data on the encapsulating resin and on the particular passivating technique used. The resin data cited by Harper represents resins which are probably similar to those used. Additional measurements are being made at NCE by another investigator to determine resistivity and breakdown voltage. The writer of this dissertation is not directly involved in this current research. The new measurements most likely will not show minute inhomogeniety which could account for greater leakage through the epoxy resin. Some further evidence of the type of leakage will be illustrated later by comparative readings of I *vs.* V for type T units compared to glass-encased units.

Type M units react to the accelerated environment in a way which contains both similarities and differences in comparison to type T units. Charts IV-5, IV-6, and IV-7 illustrate the change in the average leakage with time, the standard

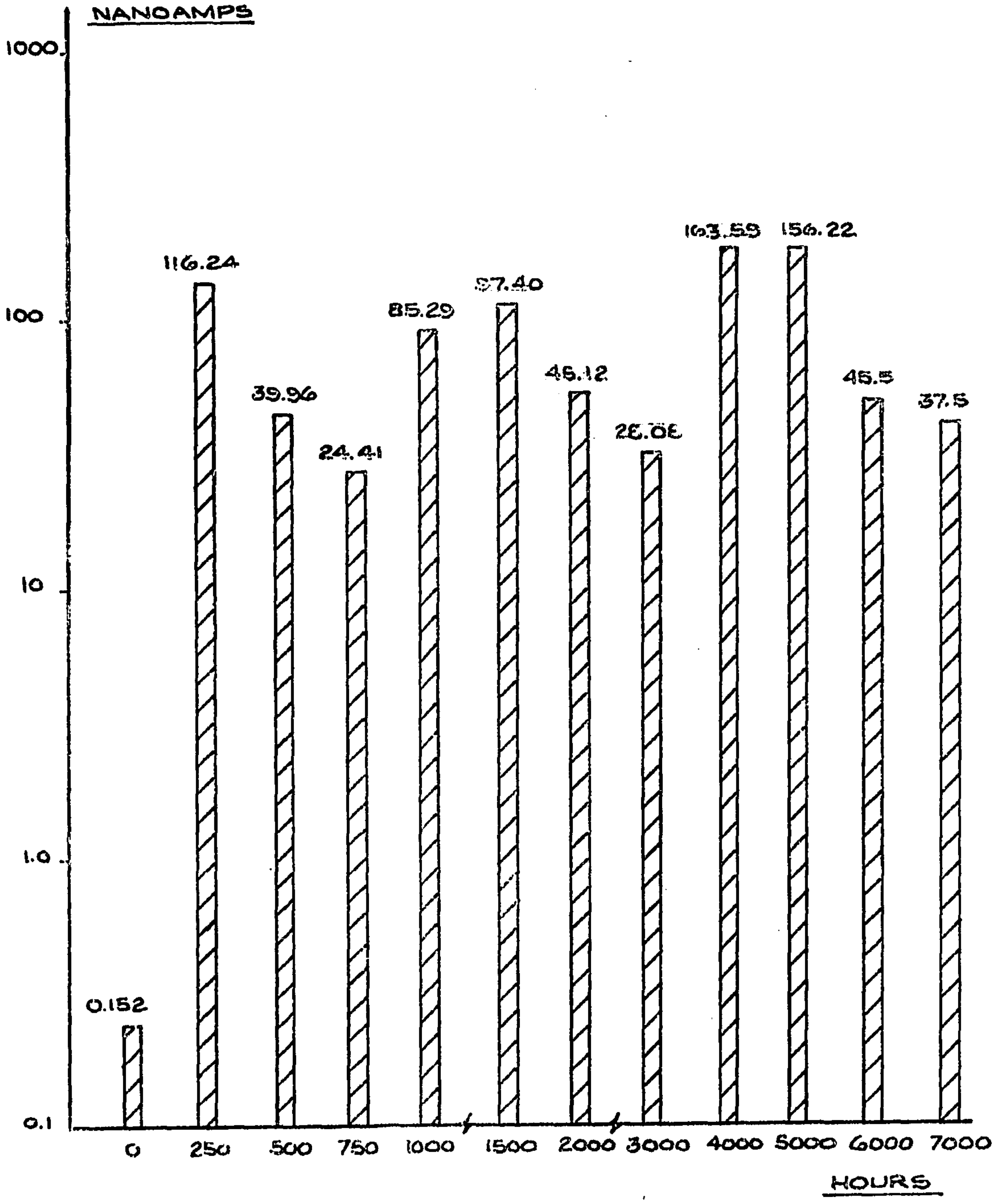


CHART IV-5 AVERAGE VALUE OF LEAKAGE CURRENT - TYPE "M" SCR

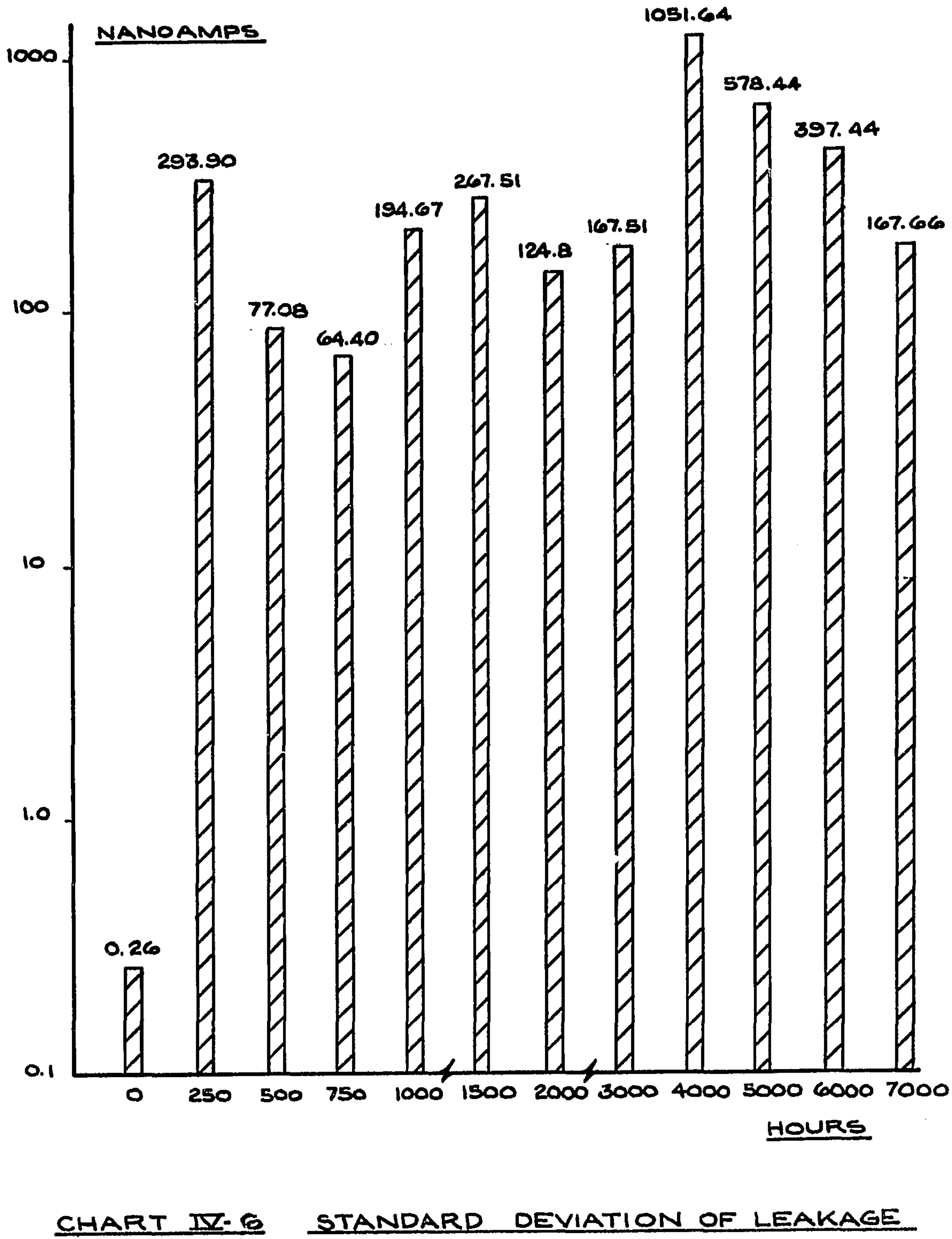


CHART IV-6 STANDARD DEVIATION OF LEAKAGE CURRENT- TYPE "M" SCR

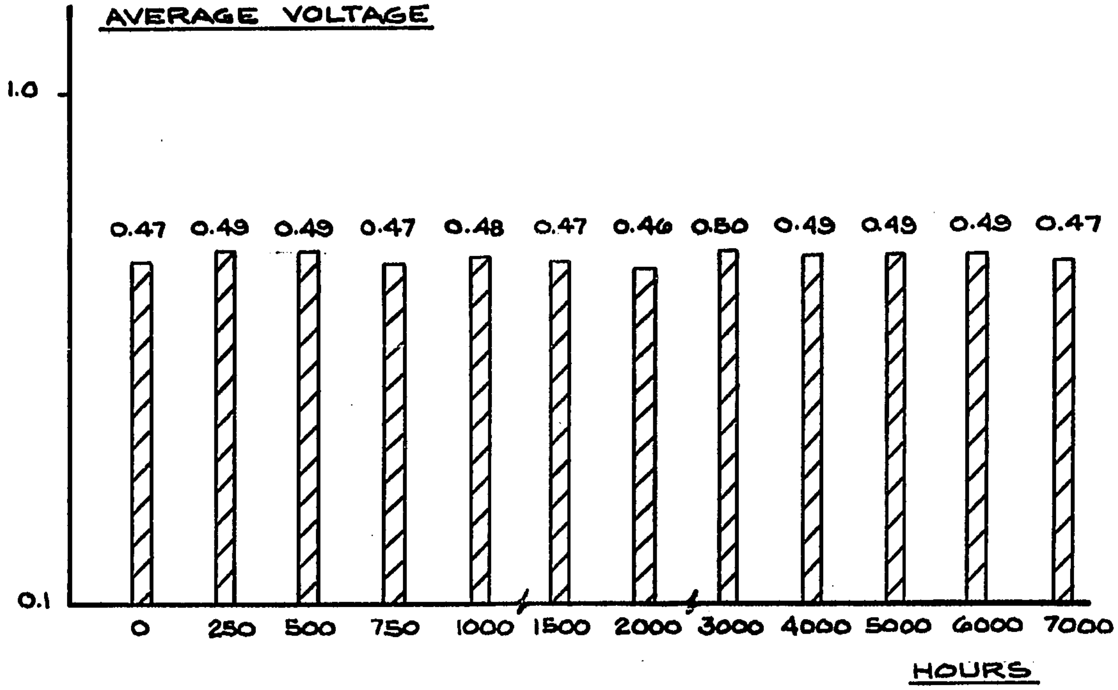


CHART IV-7 AVERAGE VALUE OF GATE TRIGGER VOLTAGE - TYPE "M" SCR deviation of this leakage, and the gate triggering voltage. There is some doubt as to the validity of the 250 hour readings for reasons not important to this dissertation.

The leakage current rise with time under the accelerated environment is much more rapid in the type M units than in the type T units. The percentage change, on the other hand, is of the order of magnitude of 1000 to 1 in both cases. The time difference to attain a condition of saturation can be accommodated by the model depicted for the type T units. If the diffusivity of moisture through the plastic is variant in the two types, an equilibrium might be reached more quickly in type M units. Further, if the depth of the active element from the surface is different in the two cases, one type will saturate with moisture earlier than the other. The plastic involved in at least one type appears to be a filled resin. Even very thin scrapings have an opaque appearance. The filler could easily account for a wide variation in the permeability by moisture. One filler-resin combination can also vary in volume resistivity from another.

The type G units represent a change in the variations of reverse current leakage with time. From time 0 to 4000 hours, the variation in average leakage current is only 3 to 1. Charts IV-8, IV-9,and IV-10 represent the average leakage, standard deviation of leakage, and gate trigger voltage as a function of time. It may also be noted that the initial readings

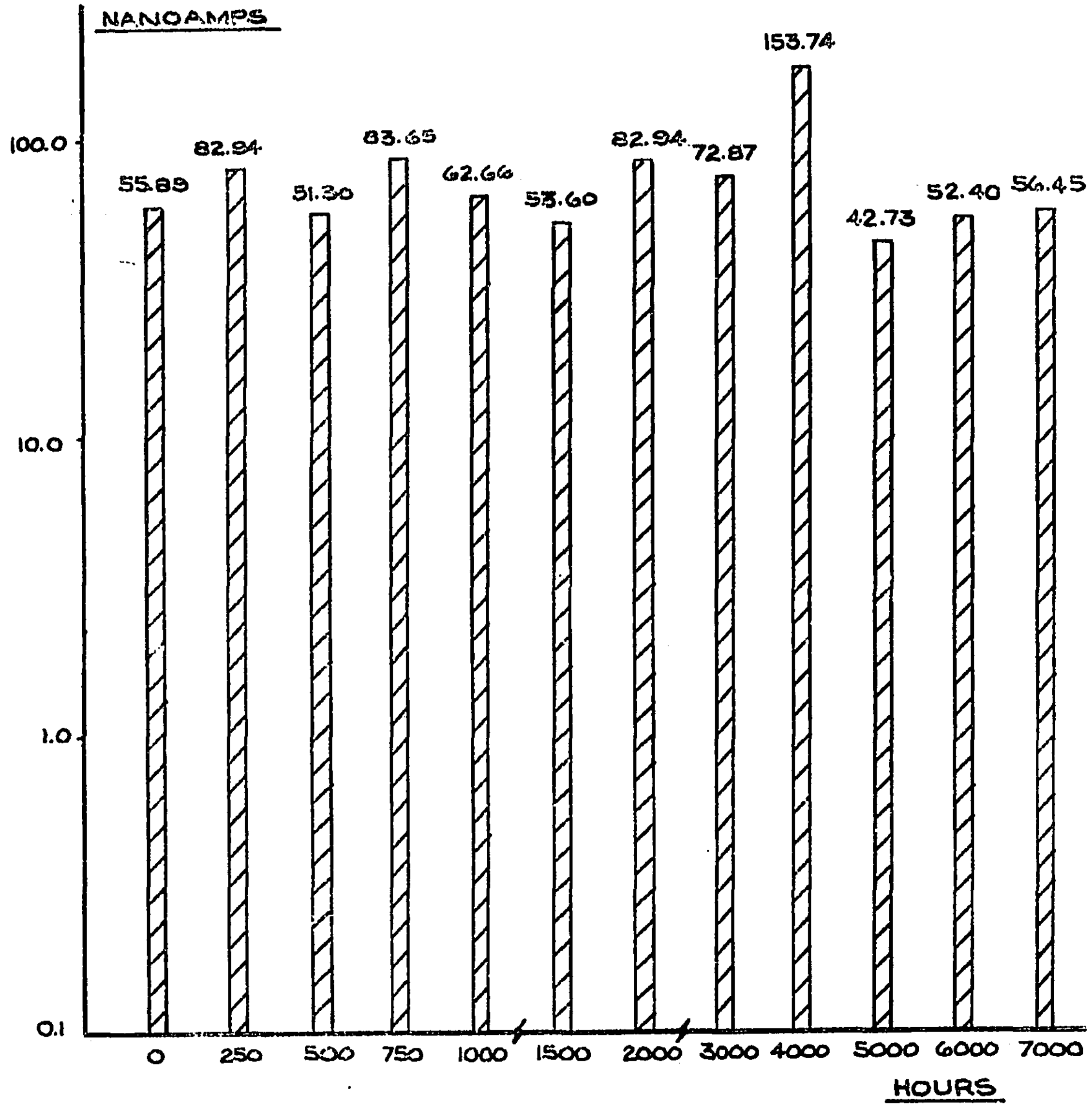


CHART IV-8 AVERAGE VALUE OF LEAKAGE CURRENT - TYPE "G" SCR

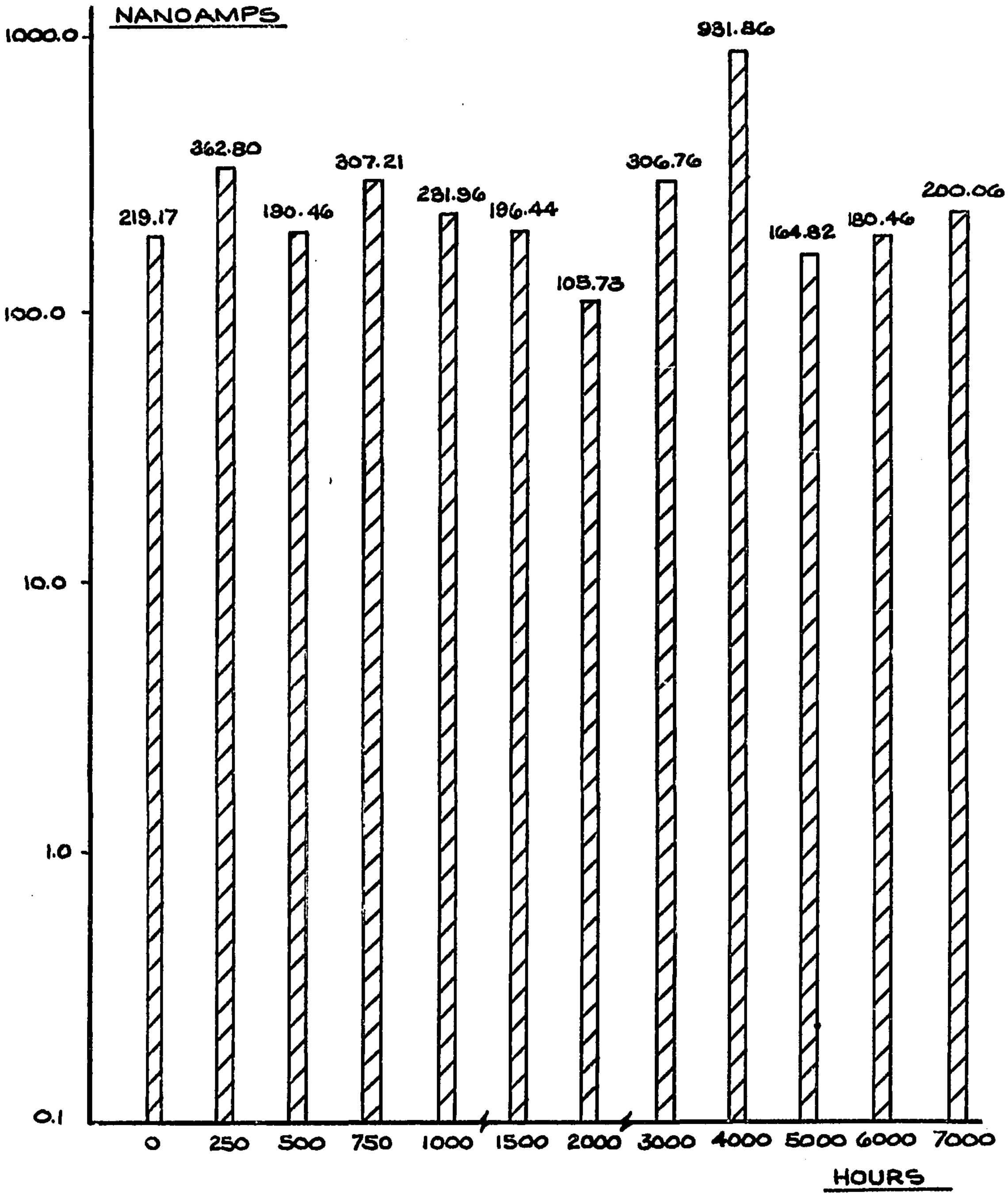


CHART IV-9 STANDARD DEVIATION OF LEAKAGE CURRENT - TYPE "G" SCR

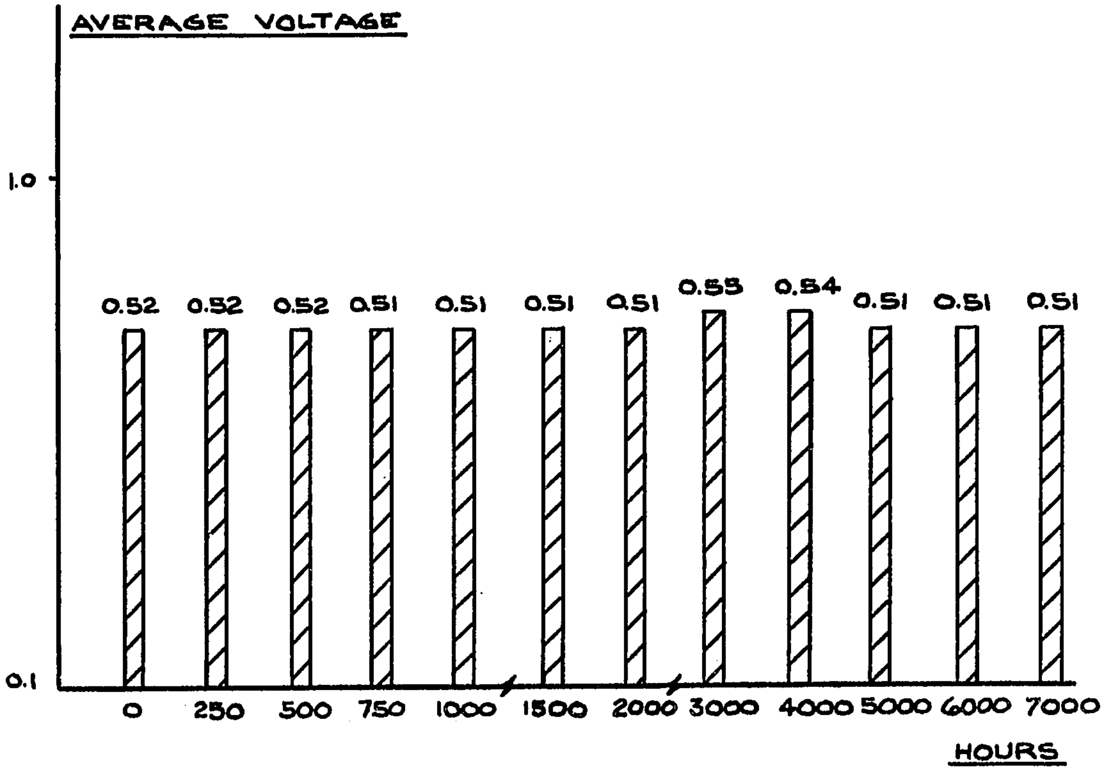


CHART IV-10 AVERAGE VALUE OF GATE TRIGGER VOLTAGE - TYPE "G" SCR are many times higher than that which would be expected of a comparable bulk diode with no surface effect.

Although in this dissertation no mechanism can be supported with sufficient data to form more than an estimate as to what might be different in type G units, a few possibilities are listed below. These may suggest to some future worker tests that could be performed with similar units to isolate the cause or causes of the apparent difference in the type G units compared to T and M units.

1. The higher initial reading might be explained in part because type G units are made for higher current applications.
2. The lack of change of leakage current with time may be the result of encapsulating with a different resin system, particularly silicone.
3. The small change might also be attributable to some pre-exposure to humidity, providing relative saturation prior to our first readings.

4. Nitride Passivated Diode Testing

A quantity of approximately 130 signal diodes were furnished to NCE by a government source for study. The primary interest in these diodes was the advertised silicon nitride passivation. An unexpected improvement in the leakage of these diodes occurred when a glass over-seal was used which also increased the mechanical strength of the diode. When originally received, the diodes were believed to be plastic encapsulated. Their appearance, Figure IV-7, resembled the plastic SCR's, Figure IV-1. The data sheets for these units, received considerably later, clearly specify the glass envelope. This glass has an importance at least during the time involved in the tests, and, as will be shown, no significant accelerated changes have occurred. Had the package been plastic, considerable physical information might have resulted in the 4000 hours involved in accelerated tests. These statements are not in any way intended to disparage the excellent life probabilities of the silicon-nitride, glass-enclosed units, but to point out that this series of tests is designed both to ascertain the durability of a particular style of protection and also to try and shed light on the mechanism of ultimate leakage.

Six assemblies, each with twenty diodes soldered to a copper strip, were coded by spacing of diodes to permit identification of an assembly as well as an individual diode in that assembly. This arrangement minimizes handling of individual diodes with the possibility of contamination of the glass. The residue left by such handling could form leakage paths around the outside of the envelope, or could cause etching of the glass surface as a result of oils and acids from the skin. Identification tabs, although used in the testing of glass passivated diodes, were not used with these signal diodes. The

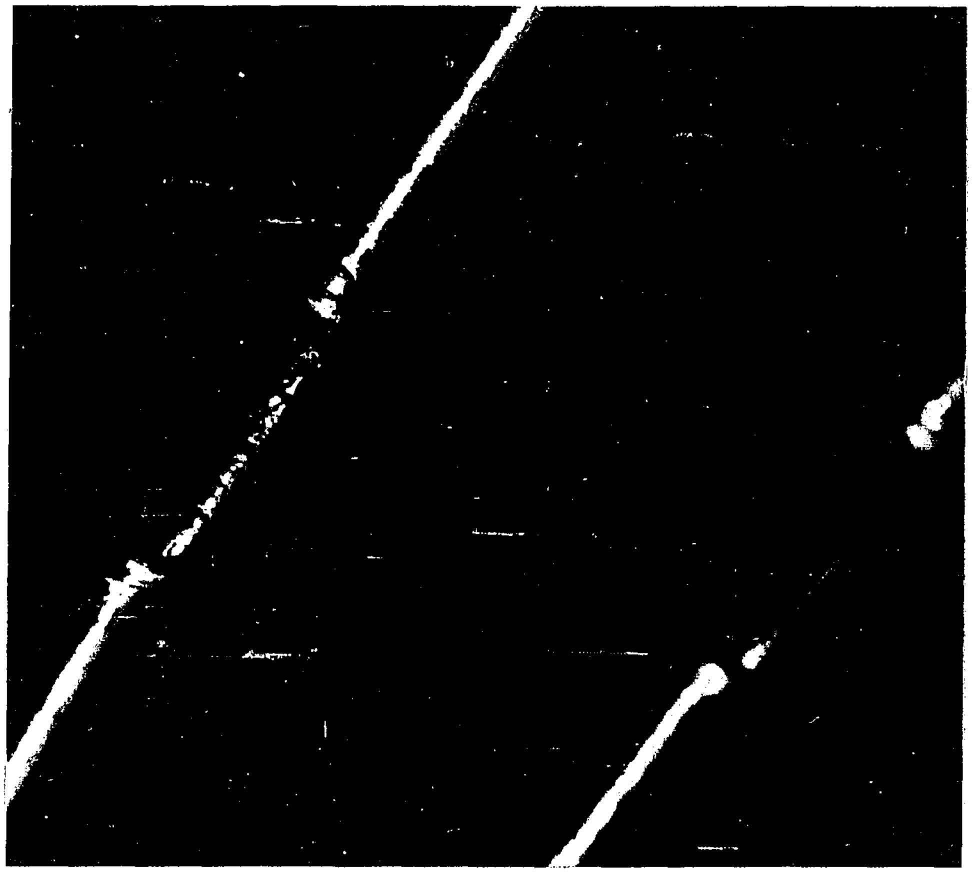


Figure IV-7. Glass Molded, Nitride Passivated Signal Diodes. Magnification Approximately 10x tabs were tolerated on the glass passivated diodes since an important part of the performance of the glass units may be related to their physical appearance including non-uniform application of the glass over-seal. Such identification tabs are likely to be a source of organic contamination from outgassing of adhesives at high temperature.

Unit number six was connected with silver solder with the diodes under water as heat protection. This was not the main purpose of the test, but this experimenter was interested in the possibilities of using water immersion as a heat sink during soldering with or without subsequent deterioration of performance. Silver solder has a strength advantage over solder. The remaining units were soldered with 60-40 rosin core solder, and cleaned in successive baths of acetone to remove the unused flux.

At zero time, the individual diodes in each unit of 20 were measured for leakage current at a reverse biased voltage of about 1/2 that required to cause avalanche. In this case, the voltage was 45 volts. After recording the readings, the diodes in units 3, 4, 5, and 6 were placed in temperature and humidity, while units 1 and 2 were kept at normal room conditions.

Leakage current was measured utilizing a General Radio Electrometer, Model 1230A. As a precautionary measure, several resistors in series totalling 500,000 ohms were placed in the circuit input to the electrometer in the event that a diode shorted. Since the normal scale used on the G.R. instrument was 10^7 ohms, the 500,000Ω in series represented only a small error in calculating the leakage current. In a parallel program tests were made on several glass passivated diodes which had such a high leakage that a resistance scale of 10^4 ohms was required. This produced a serious error in the measurement of those units, giving a much more conservative estimate of the current that would have resulted without the series resistors. In any event, where precise values were required, the actual resistance of the glass passivated units could be calculated from the voltage division. This, in turn, could be utilized to calculate the expected current if the full voltage of the source was placed across the diodes.

The 45 volts was supplied by a high voltage power supply whose input to the rectifiers was adjustable. The crude, unregulated voltage thus obtained was set accurately at 45 volts for each reading by using a 10 turn helical potentiometer. A Simpson VOM was used to measure the 45 volts for each set of readings.

Reverse current leakage readings were taken at 0 hours, 500 hours, 1000 hours, 2500 hours, and 4500 hours. The initial value on one diode was eliminated from the statistical treatment. Diode #15 in unit 1 of the diodes had a leakage of .15 microamperes; whereas the rest ranged from .007 to .034 microamperes. Diode #15 was not used in the first average or subsequent summaries.

At the outset of the test, it was expected that the leakage would increase in the temperature-humidity units and remain fairly stable in the units at normal room ambient. The presence of the excess humidity provided a known degradation of the film properties. The heat should have, in turn, accelerated the rate of water transfer through the glass or along any cracks or crevices. Moreover, the heat should have boosted the rate by which any excess monovalent ions present in the silicon nitride, the glass, or the interface between the two, migrated to the surface of the silicon. Higher temperatures should increase the rate of any other chemical reactions.

One mechanism by which increased leakage could occur in a diode if we postulate an increase of surface monovalent ions is by the creation of an inversion layer in the "p" region which would in essence increase the "p-n" contact area. This type of leakage would be characterized by very little change of leakage due to this contribution with voltage. There is a sharp difference in the case of an IGFET when compared to a diode or conventional transistor. In the field effect transistor a strong electric field exists perpendicular to the surface; whereas in the back-biased diode, a strong field exists parallel to the surface. See Figure Iv-8.

In one respect, at least, the units were not expected to deteriorate in temperature humidity, and that is, the mode

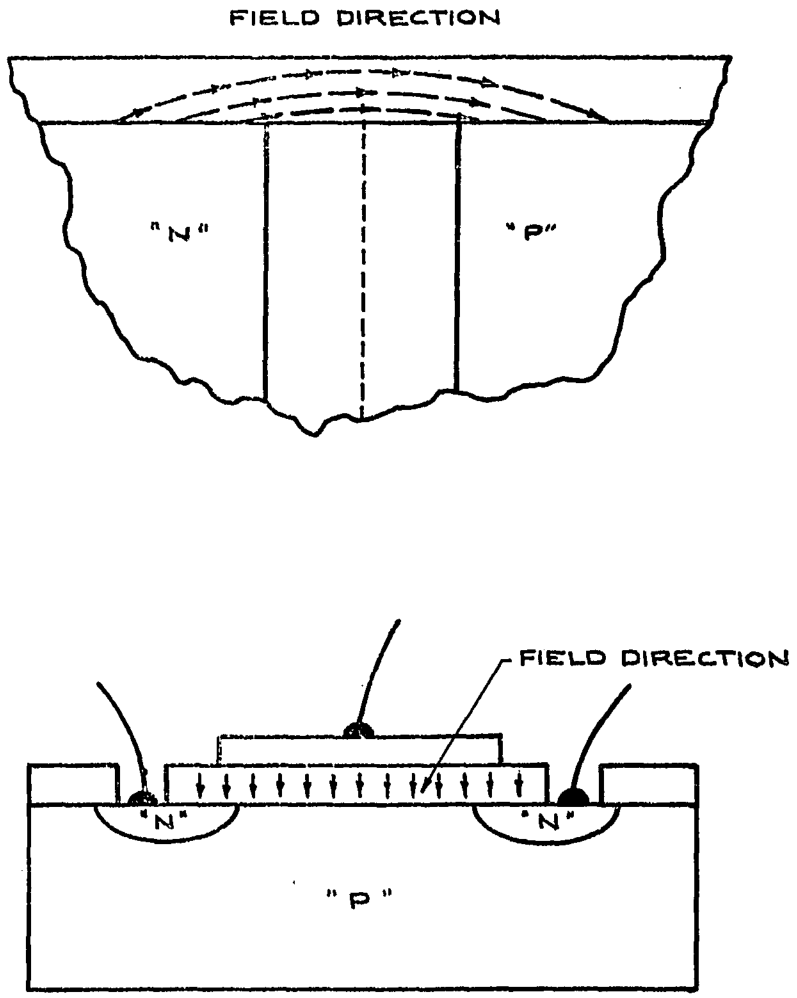


FIG IV-8 COMPARISON OF THE HIGH ELECTRIC FIELD DIRECTIONS IN A DIODE INSULATION AS COMPARED TO THE INSULATION IN AN I.G.F.E.T.

of contamination by elements originally totally separate from the diode package. This was due to the refluxing of water evaporated from the humidifier and condensing on the diodes. This not only did not add impurities, but likely extracted soluble salts (if any) from the surface and near under surface of the glass enclosure. This action will take place in any humidity chamber in which cold units are reinserted into a hot, humid atmosphere. It happened to be more accentuated in the tests run on these diodes since the chamber was an adapted coffee percolator, and continual condensation of vapor on the thin top wall is to be expected.

The tests to date cover some 4500 hours. At this point, it was hoped that there would be some trace of the separation of the control units from the temperature humidity units. Bar charts, plotted on a linear scale, show the variation of the arithmetic mean current, $\bar{i}$, with 45 volts reverse bias as a function of time. As of the initial readings, the average current of units 1 and 2 is 11.1 nanoamperes, compared with the average of units 3, 4, 5, and 6 of 11.4 nanoamperes.

The data for this test series are plotted in Charts IV-11 and IV-12. Note that the current scales are linear compared to logarithm scale for the similar plots of plastic imbedded units (e.g., Figure IV-2). The magnitude of change and the correlation of control units with temperature humidity units is displayed in these figures.

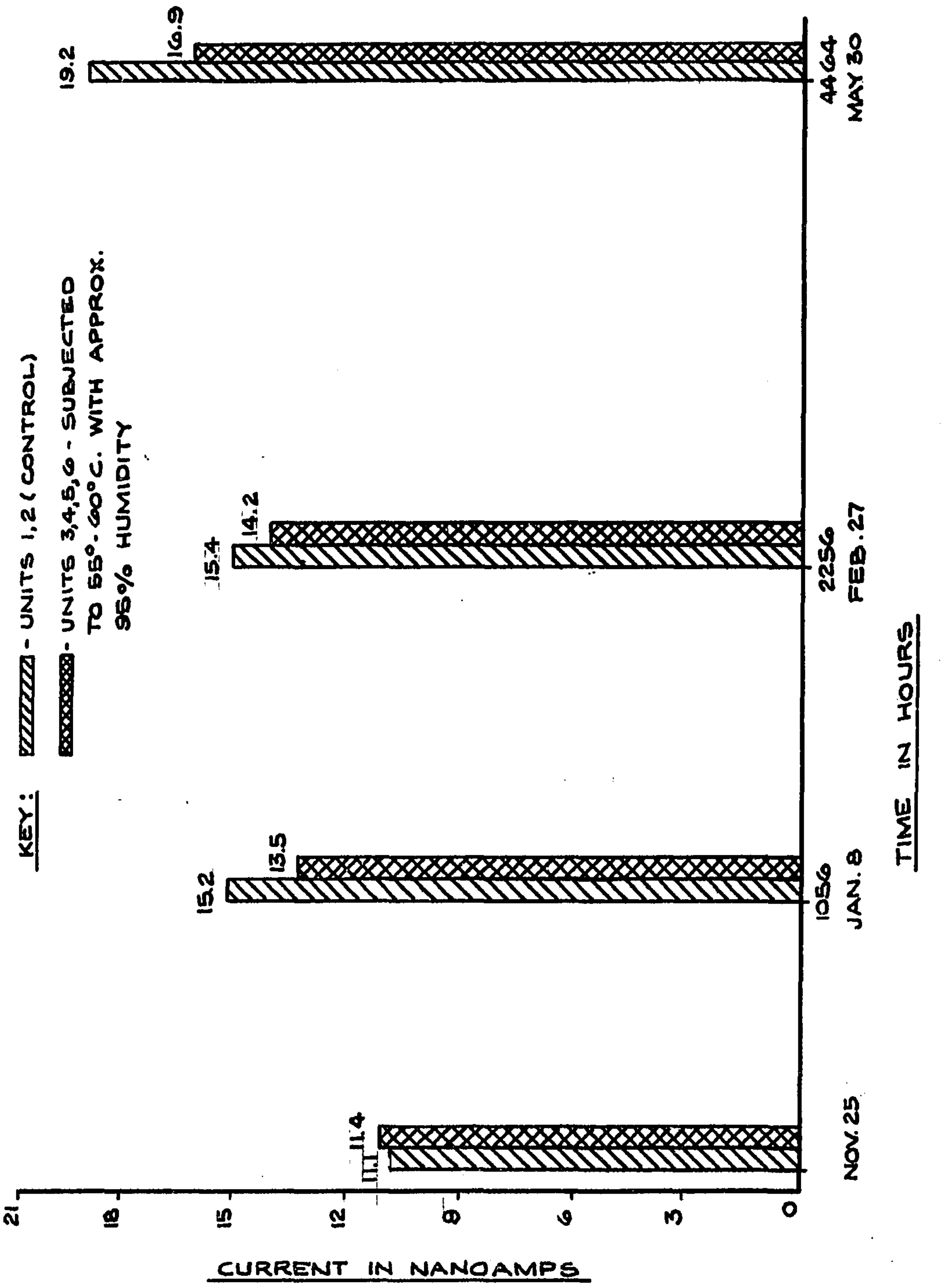


CHART IV-11 MEAN CURRENT READINGS OF NITRIDE PASSIVATED DIODES vs. TIME

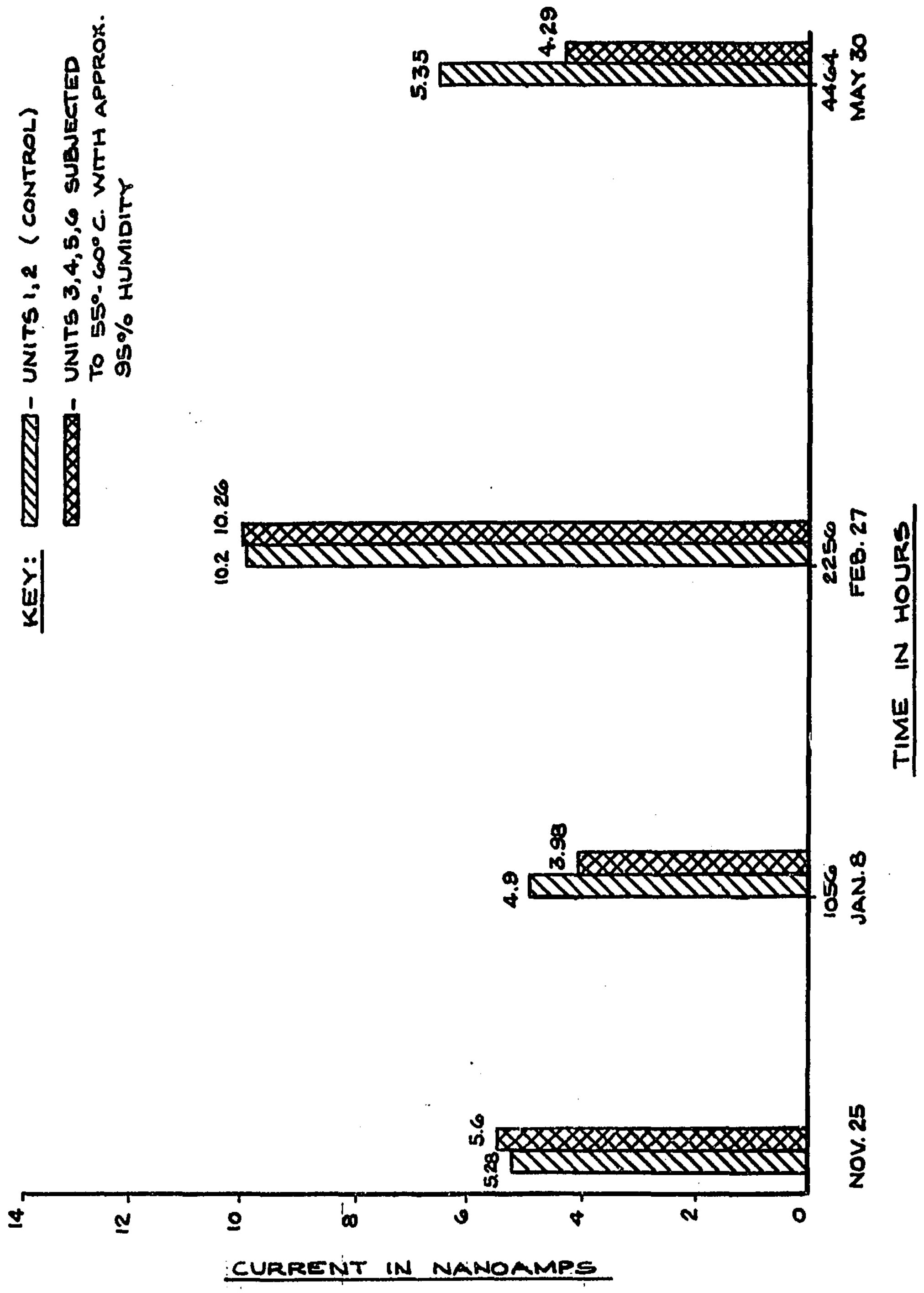


CHART IV-12 STANDARD DEVIATION OF CURRENT READINGS vs. TIME OF NITRIDE PASSIVATED DIODES

The 500-hour readings showed an unexpected drop to 7.6 nanoamperes for unit 1; whereas units 3, 4, 5 and 6 remained at 11.4 nanoamperes. At this point, some suspicion of measuring temperature effects caused the institution of temperature measurement during all further readings. The striking aspect of the data was that the individual diode readings during the 500-hour readings were for 85% of the individual readings approximately 4 nanoamperes smaller than the corresponding reading at zero hours. As it has turned out, no positive correlation of temperature at the time of reading could be interpreted to be responsible for the increment drops or rises in blocks of readings, but room temperature will be recorded and eventually controlled.

The GR 1230A electrometer was checked by the use of a standard resistor and the same voltage source used to back bias the units. The readings were consistant with a further check utilizing an RCA electrometer. Although the original purpose of these tests was to identify mechanisms of gross change of leakage, careful calibration of the meter or meters used for future readings may reveal some mechanism that is normally swamped out by large leakages in units such as the SCR units previously discussed. The very fact that the nitride-passivated, glass-encased units do not show a large change in leakage after 4500 hours of accelerated aging highlights these smaller changes as tomorrow's reliability concern.

In any event, the average current in the nitride glass-protected units which were exposed to temperature-humidity increased from 11.4 to 16.9 nanoamperes over a period of 4500 hours. The current increased from 11.1 to 19.1 nanoamperes (over this same period) for the control units.

While the field of reliability has produced examples of failure or deterioration mechanisms which diminish in rate as the temperature is raised beyond a certain point, this was certainly not to be expected of these units.

Since the difference between the average currents is (A) small and (B) in the wrong (apparent) direction, a statistical comparison was made. The standard deviation for each unit (or group of units) was calculated and compared utilizing the following formula to check the significance of the differences of the average current between units 1 combined with lack of 2, 3, 4, 5, and 6:

$$\sigma d = \sqrt{\frac{\sigma a^2}{N_a} + \frac{\sigma b^2}{N_b}}$$

Then σ_d is used with the absolute value of the difference between the means of population to compare (a) and (b); if the difference $\bar{x}_a - \bar{x}_b$ is greater than the three sigma-difference, the probability that the two populations are the same is less than the percentage area under the normal curve beyond the 3σ limit (approximately 2%), i.e.

$$C_{ab} = \frac{\left|\bar{x}_a - \bar{x}_b\right|}{\sigma_d} > 3$$

implies very strongly that the two pupulations are different.

In this case, these comparisons were made initially and then repeated for each additional reading. Table IV-1 summarizes the results to date.

Thus, there is no strong evidence to support the hypothesis that the units in humidity had behaved any differently than the units at ambient conditions.

If positive reasoning could be advanced that units 1 and 2 could not physically change in reverse current leakage, either more than or less than units 3, 4, 5 and 6 (temperature-humidity units), then perhaps the statistics could be bolstered sufficiently at this stage to draw a conclusion. Unfortunately, it is possible to provide reasoning which would support greater leakage in the control units as well as other hypotheses which would predict greater leakage in the units exposed to temperature humidity.

For example, temperature is known to speed chemical reactions in general, usually in accordance with the Arrhenius equation:

$$\text{Rate} \propto e^{-\frac{E_a}{kT}}$$

Table IV-1. Statistical Comparison of Temperature-Humidity of Test Units and Control Units Reverse Current Leakages for Nitride Passivated Diodes

Time	$\bar{I}_c$	$\bar{I}_T$	$\lvert \bar{I}_c - \bar{I}_T \rvert$	σ_{I_c}	σ_{I_T}	$\frac{\lvert I_c - I_T \rvert}{\sigma d}$
0 hours	11.1	11.4	.3	5.28	5.6	0.254
1056 hours	15.2	13.5	1.7	4.9	3.98	1.9
2256 hours	15.4	14.2	1.2	10.2	10.26	0.45
4464 hours	19.2	16.9	2.3	5.35	4.29	2.2

$\bar{I}_c$ = reverse current leakage, average, control units, nanoamperes

$\bar{I}_T$ = reverse current leakage, average, test units, nanoamperes

σ_{I_c} = standard deviation, reverse current, control units

σ_{I_T} = standard deviation, reverse current, test units where E_a = some energy of activation. A slight modification of this equation due to Eyring is:

$$\text{Rate} \propto T e^{-\frac{B}{kT}}$$

Inside layers are elements which can cause degradation (such as providing monovalent ions). The ions diffuse away from the points of concentration of contamination and, again, the diffusion coefficient acts in accordance with Arrhenius' equation

$$D \propto e^{-\frac{E_o}{kT}}$$

Clearly, temperature is likely to influence a device in such a fashion to expedite deterioration.

On the other hand, it has been mentioned earlier that the particular setup used offered the possibility of refluxing condensed water vapor over the units. This can occur by dripping from the lid, or by condensation on the units after the units are cooled during an inspection. This refluxing can cause leaching of soluble compounds in the surface, including such materials as alkali salts. Over a long period of time, we would then expect alkali ions to redistribute themselves and, hence, create general flow towards the outside of the unit, providing fewer ions near the silicon nitride-silicon transition.

Up to 4500 hours, there is no clear difference between units in temperature humidity and those at ambient conditions.

These tests are being continued, but additional tests were initiated. Units were placed in a separate humidity chamber and subjected to a 45 volt (approximately square) waveform with a 60 hertz repetition. The temperature is 65°C. Readings are to be taken each 1000 hours.

A third experimental run on the nitride protected units involves deliberately placing a field due to an external electrode at 500 volts wrapped around the glass (Figure IV-9) radially into the glass in one unit of 22 diodes and out of the glass in a second unit. This field is perhaps one per cent of the field that causes migration of alkali ions to occur in an IGFET in a few seconds, but should cause an effect over a period of 500 hours if migrations from outside in (or vice versa) is causing any influence on these units. This longer time period should also help to verify whether any voltage (field) threshold exists for migration of ions. If no apparent effect occurs over the first 1000 hours, the field will be increased, and after 2000 hours increased again if necessary. Theoretically, it would be better to start out with a high voltage initially (say about 10,000 volts) but, practically, this would run the risk of destroying the encapsulating epoxy resin which was used to hold the metal foil in place over the glass body of the diodes. The epoxy would stand the voltage, but an air bubble between the metal foil and axial lead could easily be present.

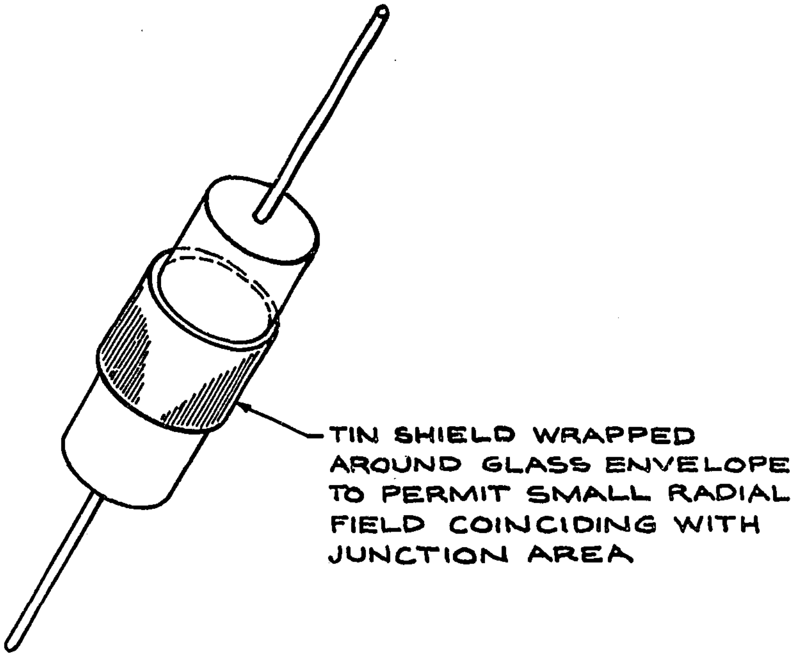


FIG. IV-9 RADIAL FIELD APPLIED TO SILICON NITRIDE PASSIVATED UNITS

An examination of plots of the standard deviation, σ , with increasing time does not show a clear cut trend. See Chart IV-11. If a mode of leakage failure had taken place, a spread in the current readings would be anticipated. Since this did not take place in an observable fashion, additional assurance is present that a failure trend was not in evidence after 4500 hours.

There is a general increase in back leakage of these silicon passivated, glass-encased diodes. The increase is independent of the temperature and humidity conditions of storage, at least insofar as those limits to which these units were tested. This writer does not ascribe any particular mechanism as the cause for this change. This is not due to any lack of possible physical occurrences which could cause the change in leakage, but because each of these would respond rate-wise to the higher temperature under the humid conditions.

The drifting of both the accelerated units and control units limits the usefulness of comparative readings of diodes in each of the two sets such as the variations of current with applied voltage. Such voltage readings were taken at about the 3600 hour point by which time it was apparent that control units and accelerated units were changing together, although very slightly in extent.

5. Comparison Between Manufactured Types

With the glass passivated diodes, no control set was retained because of the limited quantity of diodes, and one diode was tested prior to humidity to determine the relation of voltage to current up to one-half breakdown voltage. Two factors prevented this from adding to our knowledge of the change or current paths or elements with accelerated environment. First, the unit so tested suffered an almost complete degredation by the 500-hour reading. Second, these units differed from the nitride passivated units in that those units which did not degrade markedly also did not, in general, shift upward in leakage.

Despite the inability to pinpoint the cause of the very small change in leakage in the silicon nitride passivated diodes, it is still useful to display on one curve the current voltage relationship of high leakage epoxy units compared with nitride passivated units and glass passivated units. Since the range of conductivity is widely spread among the types of units, the voltage and current scales are arbitrary. Figure IV-10 displays one glass passivated unit, one nitride passivated diode, and two silicon controlled rectifiers. The two SCR's demonstrate a once repeatable nonlinearity with increasing voltage which is approximated by a piecewise linear curve. Since an SCR contains two forward biased junctions with variable injection efficiencies, the higher slope curve may represent some phenomena connected with changing α of

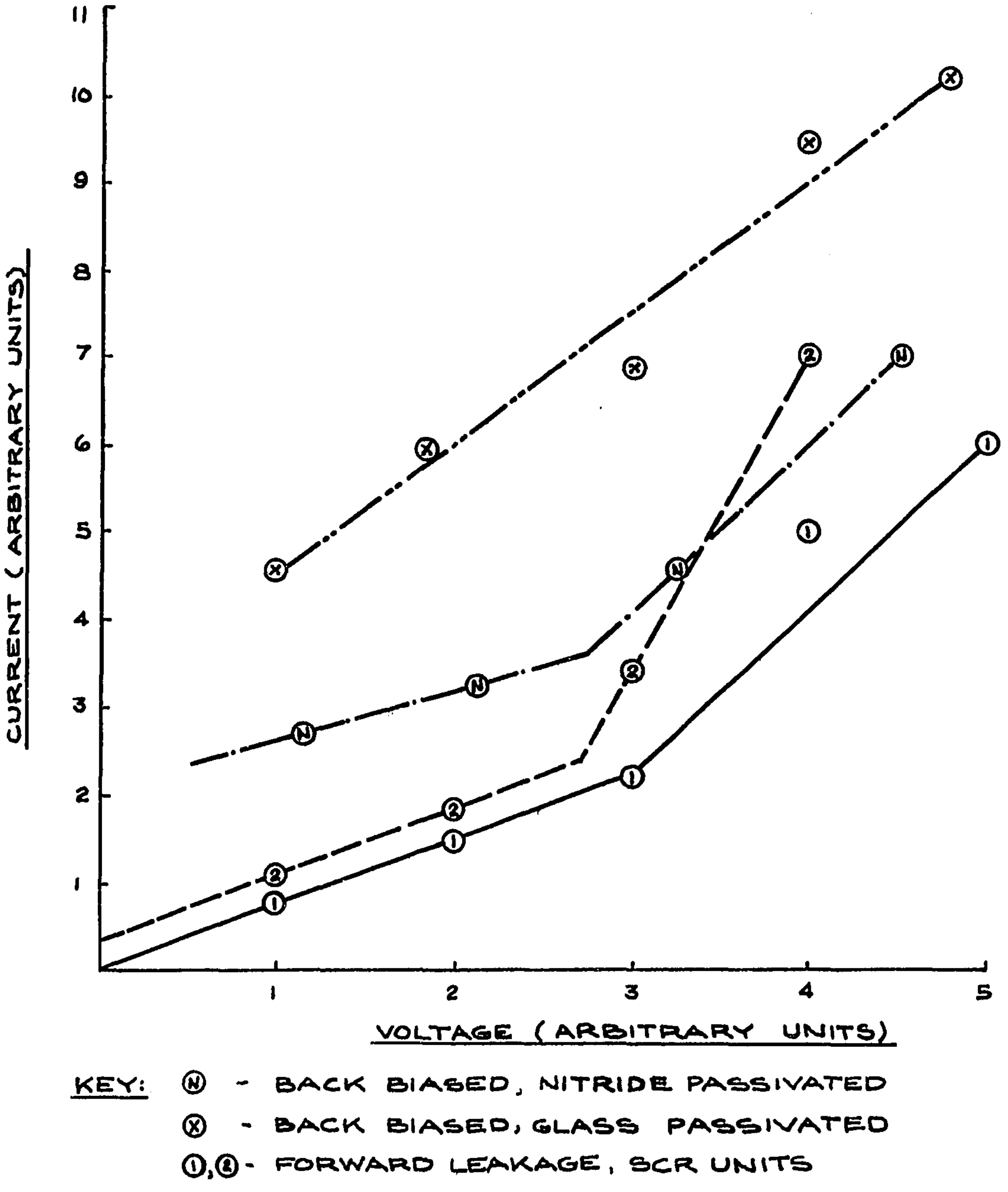


FIG. IV-10 . PLOT OF VOLTAGE vs. CURRENT AFTER HUMIDITY FOR VARIOUS TYPES OF UNITS either or both forward junctions as the surface leakage increases. Another possibility is that the passivating film is approaching a region of avalanche, and that slope from the break point toward higher voltages represents the lower resistance of essentially only the paths in the resin-oxide interface.

An interesting aspect of the various curves is the greater tendency of the current-voltage curves to approach the origin in the epoxy units. It should be noted that in the epoxy units measured, the leakage was three orders of magnitude greater than the leakage current of the same unit prior to accelerated testing. With such an occurrence, it is expected that any normal back bias leakage would be completely masked, and the curves agree with this assumption.

In the case of nitride passivated units, the leakage scarcely changes after temperature humidity, and an extension of the voltage-current curve to the current axis gives a very clear indication of a current intercept which will probably be very close to the bulk back bias current leakage. The zero voltage, zero current reading on each of these units was, of course, not used. The magnitude of leakage, not given here, was of the order of the expected leakage for a silicon diode reverse biased.

The voltage-current curves are approximated by a fixed I_0 current with a near linear portion adjoining if the model of the prior paragraph is correct. The linear portion may be considered resistive in nature, but no supplementary data exists that points particularly to the mechanism. As an educated guess, it would probably be leakage on the surface of the silicon nitride and through the nitride at each side of the depletion layer. At the end of this chapter, a section will be devoted to additional tests that might lead to clues regarding the nature of the leakage in these units.

6. Glass Passivated Diodes

Comparison has been made of resin molded units with nitride passivated units and glass passivated units, but individual discussion of the glass passivated test units is yet to be made. The entire test run of this type of diode utilized 25 units. No control sample was withheld as a result. The small sample was not the main distinguishing feature of this run of diodes. Of the 25 units, eight were broken or found broken during the first 4000 hours of running. The general appearance of this type is illustrated in Figure IV-11 and the remnants of a broken unit in Figure IV-12. These units were not constructed with full production tooling, and, as a result, many visible defects or differences in appearance resulted. The two central units in Figure IV-11 illustrate this very well. The unit on the right covers an equal portion of the upper and lower electrode; whereas the unit in the center of the figure covers almost all

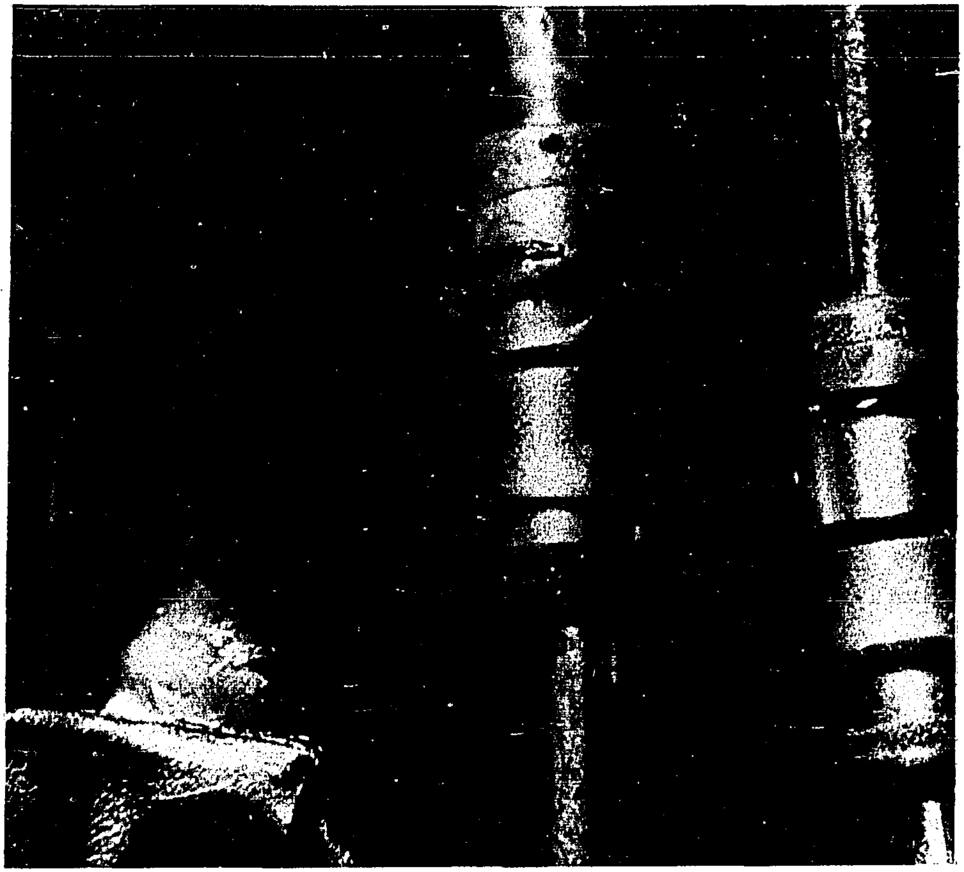


Figure IV-11. Glass Passivated Diodes, Glass Sealed. Aluminum identification tag is visible in lower left corner. Magnification approximately 10 x

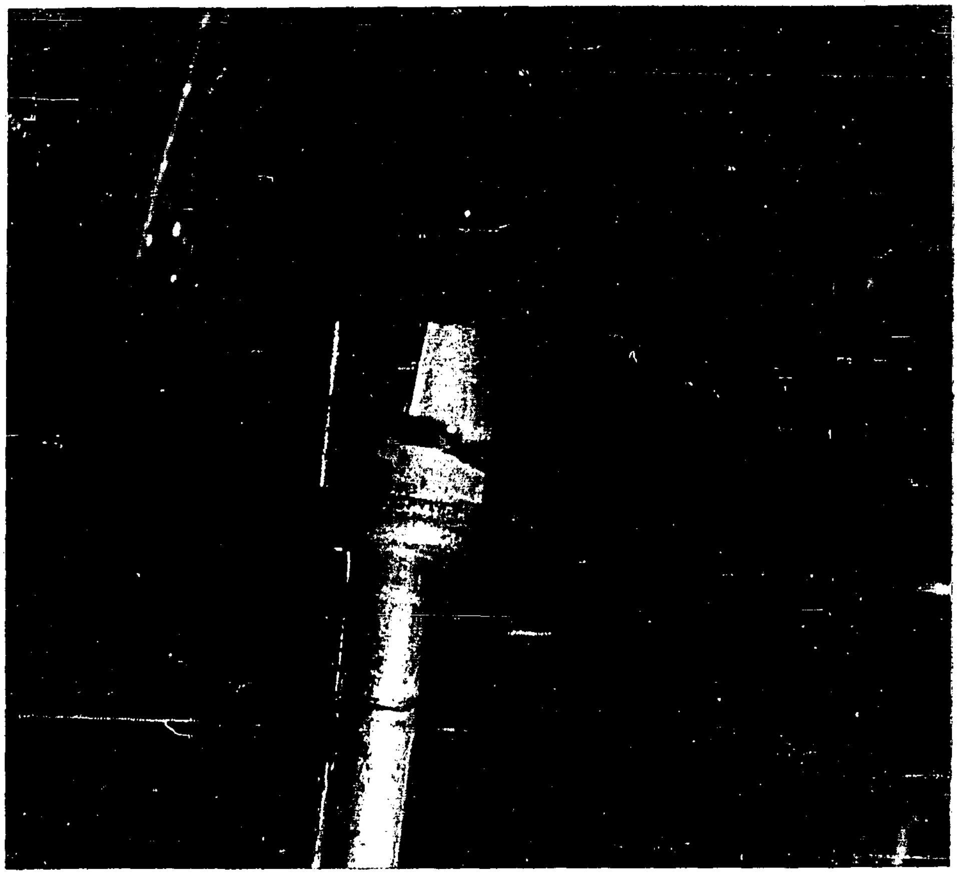


Figure IV-12. Shattered Glass Passivated Diode. Magnification Approximately 10 x of the bottom electrode and very little of the top. The top edge of the glass on this upper unit is ragged.

A more complete list of visible defects appears in the Appendix to this dissertation. Every unit with visible cracks fell apart physically during inspection, assembly of the sample unit, or prior to the first 1000 hours of accelerated testing. Other units also cracked, some of which might be traceable to visible defects noted at the start of this test run. As noted earlier, the total lost by catastrophic physical separation was eight.

Of the surviving units, an additional seven units deteriorated so badly in leakage that an increase of three orders of magnitude occurred. It is postulated that moisture has completely penetrated these units.

The ten units which did not shatter or suffer a thousand-fold change were very well behaved. The worst case of the ten resulted in change in resistance of two to one. Six units were virtually unchanged in leakage, and three slightly changed.

The essential difference in the test performance of the glass passivated diodes and the type T or M plastic molded diodes is the fact that in the case of the glass passivated diodes, many of the units which failed or deteriorated have assignable causes for such failure. There is a striking similarity in that some units of each type did not degrade to any great extent.

Carrying this similarity to the extreme, another speculative model of failure in the epoxy units is outlined forthwith. Glass molding of a protective case is not entirely dissimilar to compression or transfer molding of a resin. In both cases, a hot, viscous material is involved, which must be forced into the finally desired shape by compression or pressure technique. If a filled plastic is involved, as is believed to be the case in the types of diodes tested at NCE, any defects which occur are likely to be hidden defects. On the one hand, the clarity of a glass diode may be illustrated in Figure IV-11 in which defects are readily visible. This is not apparent from Figure IV-7, the nitride passivated units, in which the glass has been coated with an opaque enamel. However, two of these units have been examined after removal of the enamel coating, and a clear, bubble-free, uniform glass molding is revealed, well bonded to each terminal.

No such evidence, pro or con, is instantly visible in the molded plastic units. It is the experience of this writer, however, that the usual irregular shaped filler particles of plastic tend to entrain tiny amounts of air in the final resin mixture. Hence, minor porosity is expected, and major flaws, such as might be visible in glass units, are likely to be obscured. The presence of mold release (if used) in the case of a resin encapsulation is likely to increase the probability of a path all of the way into the silicon chip of the diode.

The existence of major porosity or faults in glass or plastic provides a mechanism for moisture retention through adsorption that is considerably faster than the bulk absorption in a flawless assembly.

7. Recommendations for Future Tests

Through the help of Chapters II and III, the tests in this chapter have provided a better understanding of high leakage units. To gain a similar understanding of the mechanisms present in such low leakage units as the nitride passivated, glass-encapsulated units will be of use at such time as a doubling of initial leakage is defined a failure.

Ideally, it would be desirable to obtain full production units with combinations of protection variant from those tested previously. In particular, the following styles are desired: molded epoxy diodes with a nitride passivation and silicon dioxide passivated diodes in a smooth, bubble-free glass encapsulation.

Voltage-current curves should be taken at the start of each run on a sample of each type unit. The tests should include low temperature storage to minimize even the small drift of the nitride passivated, glass-enclosed units.

The units should be obtained in sufficient quantity to permit: (1) one set of units stored in a dessicator at low temperature (- 60°C), (2) one or more sets of units at room temperature, (3) several sets of units under temperature humidity, and (4) several sets of units at various temperatures with humidity low.

If the axis intercept of the voltage current plot goes up with time under any of the above conditions, an indication of stretching of the apparent junction area is evident. On the other hand, if the slope of the 1/R line increases, the occurrence of increased leakage is indicated. If the latter event occurs when humidity is present, and does not take place when humidity is absent, conclusions can be drawn as to the surface nature of the increased leakage.

REFERENCES

[1] Army Contract #DAAA-21-68-0-0500 - Progress Reports 1 thru 12. The designation M, T and G units is using the designation used in this report.

[2] Mathes, K.N., "Electrical Properties of Polymers," General Electric Research and Development Center, General Chemistry Laboratory, Schenectady, New York, Report Number 67-C-257, June 1957.

[3] Harper, Charles A., Electronic Packaging with Resins, McGraw-Hill, 1961, p 71.

CHAPTER V

INFRA-RED INTERACTION WITH SILICON AND PASSIVATING LAYERS

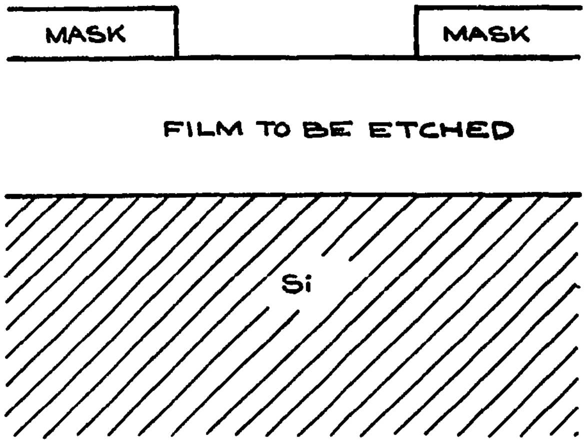
1. Introduction

In Chapter III the absorption of energy with a wavelength of 10.5 microns in silicon and the principal primary insulating layers was discussed. The purpose of the introduction at that point was to show the usefulness of this important phenomenon and the interplay of the other physical constants [thermal conductivity, specific heat, latent heat of vaporization, melting point, and optical index of refraction]. It is the purpose of this chapter to more fully discuss the potential uses of this phenomenon. The ultimate interest is device reliability.

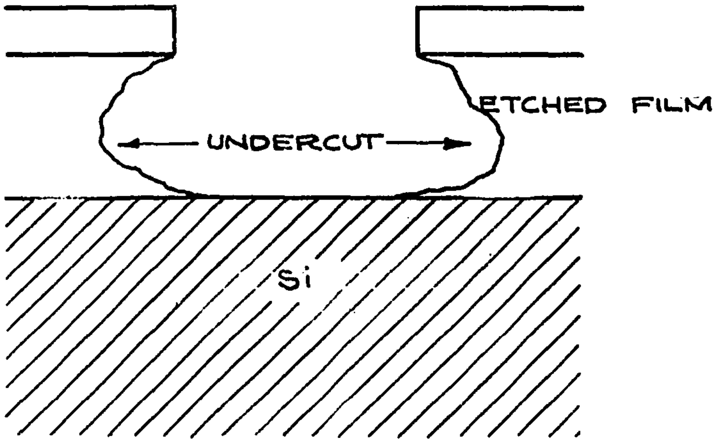
2. Insulating Film Removal From Silicon Substrate

The specific case discussed in Chapter III was the removal of an insulating film from a selected spot on a silicon surface. This is a necessary procedure in silicon wafer processing to produce masks for the diffusion of impurities into the silicon wafer to produce "n" and "p" regions. The predominant technique now being utilized involves chemical etching. Three disadvantages to the current technique are (1) silicon nitride is difficult to etch; those chemicals which will remove silicon nitride place stringent requirements on the masking film, and (2) etching through a mask generally undercuts the surface below. See Figure V-1. (3) The use of strong acid etches on insulating layers opens the possibility for adsorption of ions which will prove undesirable in the completed unit. Under some circumstances, minor porosity may occur and this effect will be accentuated.

The original experiments on film removal from a silicon wafer were made utilizing a CO_2 Laser specifically constructed for the purpose of producing intense beams at a wavelength of 10.5 microns. See Figure V-2. This wavelength radiation is absorbed heavily in the silicon dioxide and very little in room temperature silicon. The first experiments were conducted in a normal room atmosphere with a stream of Argon directed on the wafer to prevent re-oxidation of the silicon surface. As the film was moved (by hand) slowly through the beam focus point, a definite track appeared which looked like an indentation of the silicon surface. On the second try, the wafer cracked. The partial success of this experiment is attributed to the slow movement and low power of the CO_2 Laser at that time. The rough calculations in Chapter III show clearly that at increased laser power, only a small fraction of a second is involved in the evaporation process. Continued exposure to the beam will eventually heat the silicon, in all probability increasing its coefficient of absorption, α .



(a) PRIOR TO CHEMICAL ETCH



(b) AFTER ETCHING OPERATION

FIG. V-1 CHEMICAL ETCHING THROUGH A MASK SHOWING UNDERCUTTING ACTION OF THE ETCH.

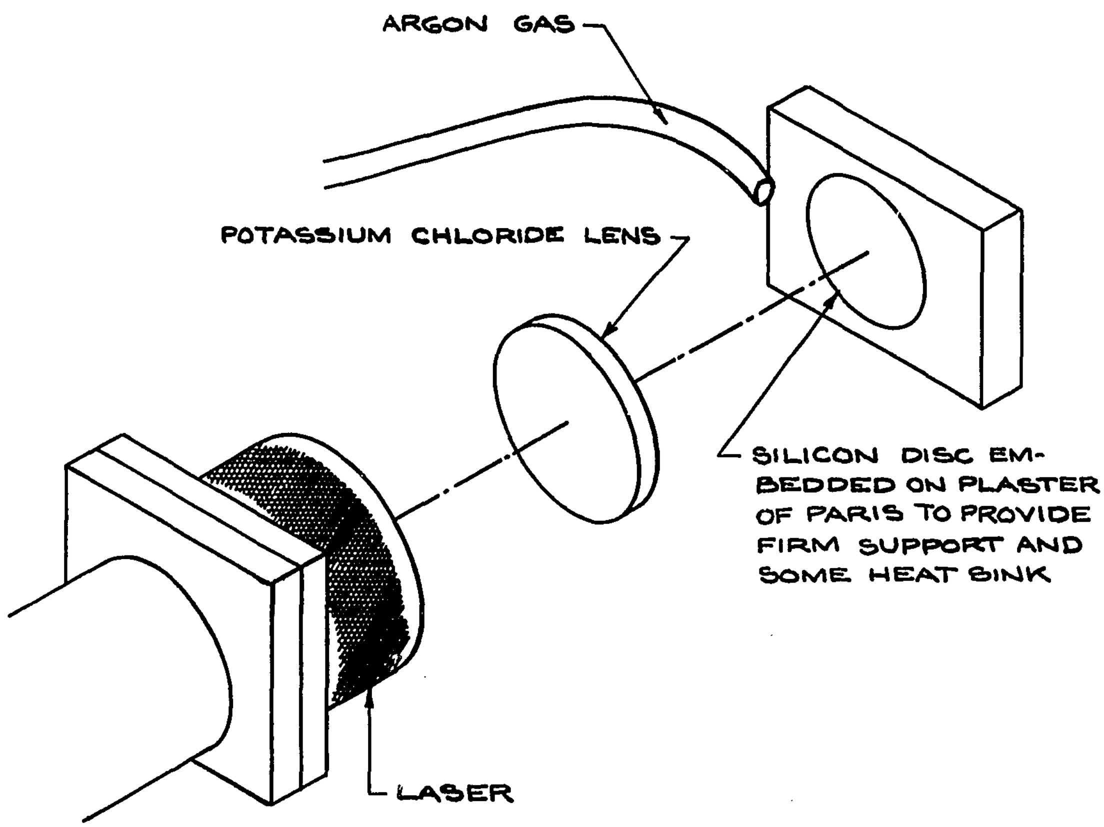


FIG. V-2 ORIGINAL EXPERIMENT ON FILM REMOVAL FROM A SILICON WAFER

This does not pose a permanent problem since lasers can easily be pulsed to give a burst of energy for a specified period of time.

A second factor might be the heat removal by convection, which was not considered in the calculations to date. Future experiments are planned with the coated wafer in a vacuum. The vacuum collar has been fitted with an external-internal slide mechanism that will permit manipulating the sample from outside the vacuum. A more intense beam and faster movement will be employed. The use of a vacuum in the range of 10^{-5} to 10^{-6} will eliminate heat transfer by convection.

A related process using lower energy levels is also postulated. Using a gaseous etch environment, the silicon wafer is heated by radiant energy only where insulation is to be removed. The gaseous etch may, of course, be adsorbed on the remaining insulating layer.

The elimination of adsorbed or absorbed ions would improve the surface resistivity by a great factor. A striking example of this is cited in the Handbook of Chemistry and Physics[1] in which fused quartz varies from 2×10^6 ohms per square to 3×10^{14} ohms per square depending on cleanliness and humidity. Since surface resitivity is of prime importance in

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[1] Hodgman, Charles D., Handbook of Chemistry and Physics, 40th Edition. Cleveland, Ohio: Chemical Rubber Publishing Company, 1959.

the case of the silicon dioxide passivated, epoxy molded SCR's tested in Chapter IV, the infra-red evaporation technique is seen to be valuable.

3. Evaporative Coatings by CO_2 Laser

(a) Silicon Nitride

In Chapter II the Arrhenius equation was shown to hold for a wide range of chemical reactions. It will be recalled that the rate of reaction is proportional to:

$$\text{Rate} = K\, e^{-\frac{E_A}{kT}}$$

where E_A - an activation energy

This equation applies to molecular disassociation as well as molecular formation. It would be expected that a compound which decomposes thermally would proceed at some rate governed by the temperature. Such a compound when heated conventionally by such techniques as evaporation from a filament or boat would probably be at a very high temperature for a substantial time before reaching the evaporation stage. Under such circumstances, deterioration is likely to occur.

On the other hand, if a particle of this substance is subjected to radiant energy of extreme intensity, evaporation occurs almost instantly and the likelihood of decomposition is diminished. Future experiments are planned to attempt to evaporate silicon nitride by this technique.

The importance to the ultimate electronics package can be very great. If silicon nitride can be evaporated successfully, a simple method will now exist for depositing successive layers of silicon nitride and silicon dioxide. Two material sources can be alternately irradiated, and the desired thickness of each can be deposited on the cooler silicon substrate. The proportions of each layer can be adjusted to give a low stress silicon-insulator interface. This film would be subject to little difficulty with sodium migration.

Techniques now exist for co-depositing two materials, but the resulting mixture will not have all the desirable features of the individual films. In the instance of silicon nitride, even a slight mixture of silicon dioxide will greatly reduce the ability of the composite film to resist diffusion.

Figure V-3 shows how the CO_2 beam was introduced into the vacuum system, and Figure V-4 shows the construction of the sodium chloride optical window which has been utilized.

(b) Silicon Dioxide

Experiments have been conducted at Newark College of Engineering evaporating silicon dioxide into a silicon wafer. A thick aluminum foil holder for the silicon was utilized, which

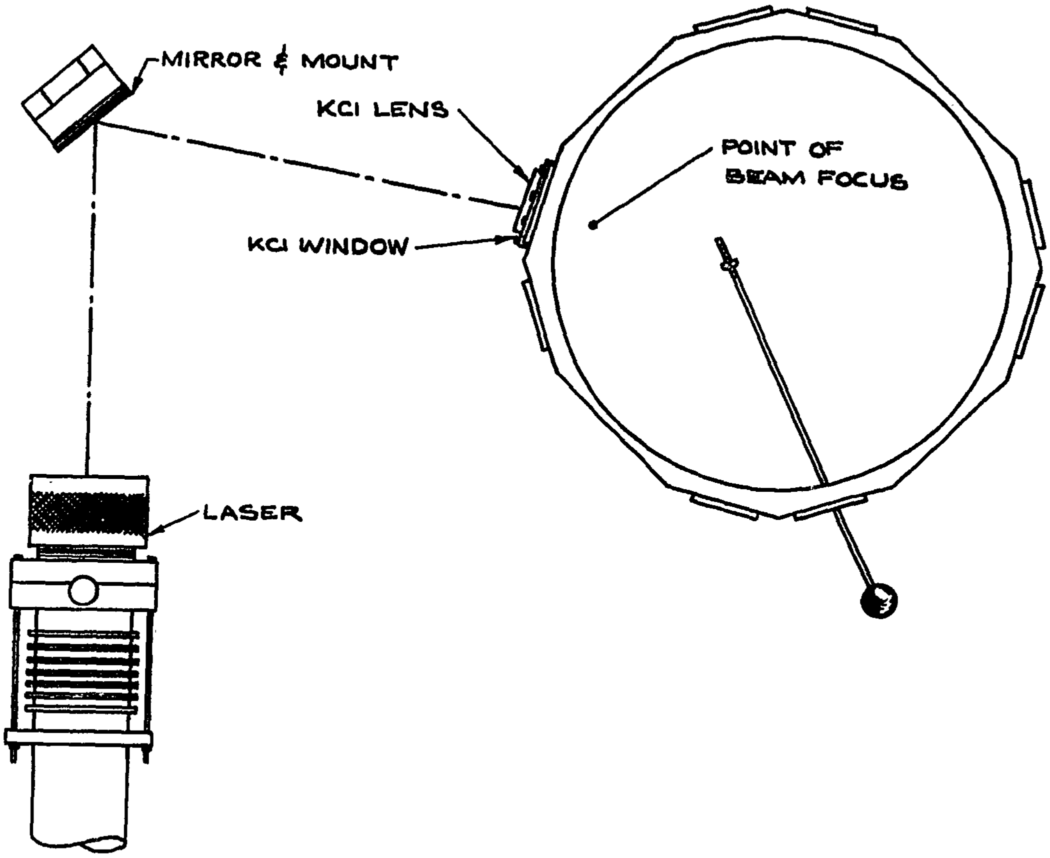

FIG. V-3 DIAGRAM OF ARRANGEMENT FOR INTRODUCING A CO_2 LASER BEAM INTO A VACUUM SYSTEM.

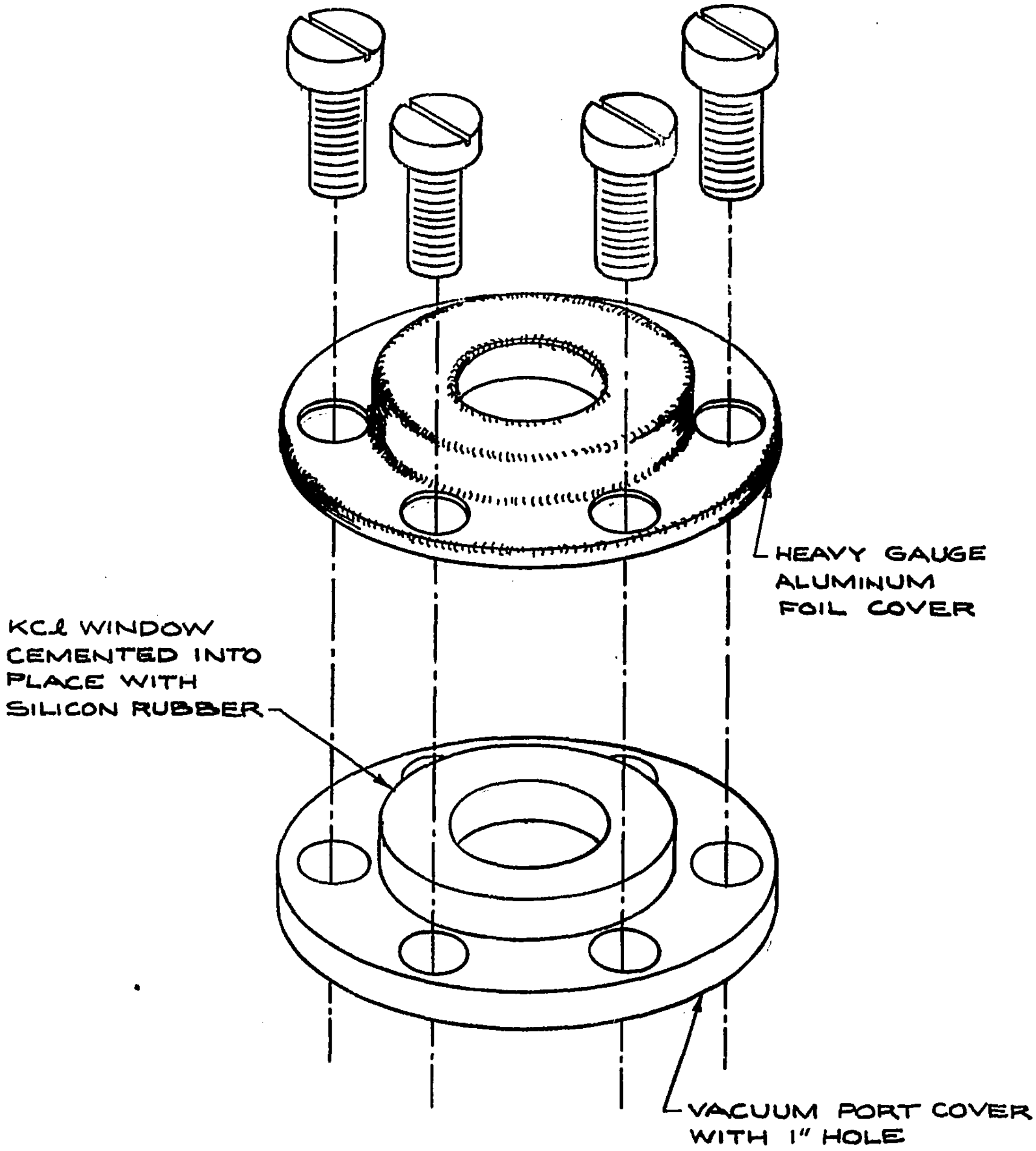

FIG V-4 SODIUM CHLORIDE WINDOW FOR VACUUM SYSTEM.

was bent over the edges of the silicon wafer, thus providing not only support, but shielding under the folded area from the evaporated emanations of silicon dioxide. This shielding is useful for determination of film thickness. Figure V-5 shows a diagram of this holder.

The resulting film after several seconds of evaporation was found to be approximately 13,000 Å thick by directly weighing the film. The rate of deposit was so high that the film did not adhere to the silicon substrate. Thinner, adherent films were found on the same piece of silicon, out of the direct line of travel of the main beam of silicon dioxide. The very high rate of evaporation has a reliability significance. Any vacuum system is subject to impurities, and the slower that any evaporation is carried out, the greater the probability of adsorbtion and subsequent covering of these impurities on and in the final film. The adherence problem can easily be solved by reducing the substrate to the temperature of liquid nitrogen.[2] Figure V-6 shows the dishing of the powdered silicon dioxide that limited the extent of silicon dioxide coverage. Between the areas of poor adhesion and good adhesion is a region in which something akin to spokes of poor adhesion extend into the good adhesion region. These spokes, Figure V-7, are indented at uniform intervals, with a

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[2] Sohn, Kenneth, Private Communication, Newark College of Engineering, September, 1969.

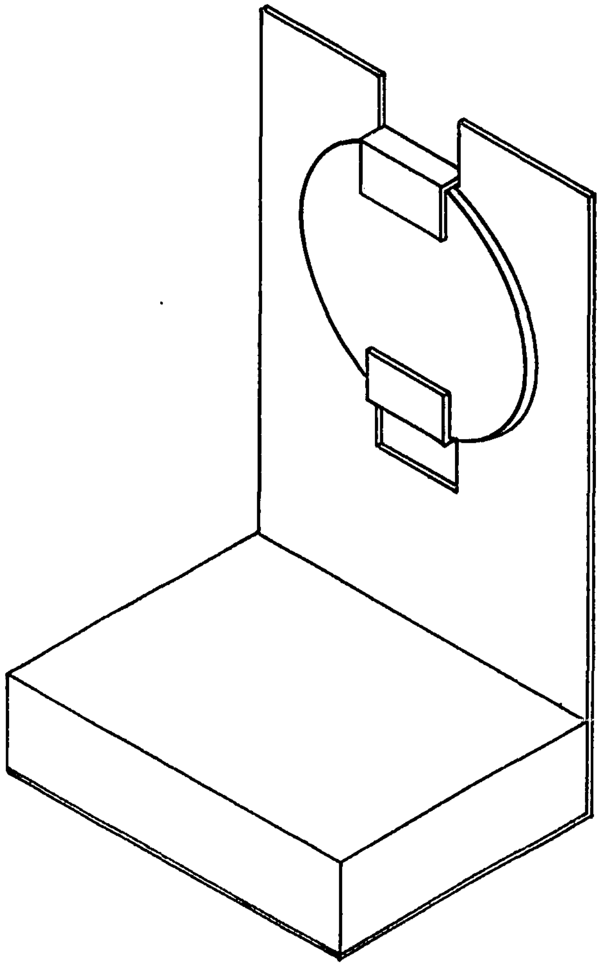

FIG. V-5 ALUMINUM HOLDER FOR SILICON WAFER DURING SILICON DIOXIDE EVAPORATION.

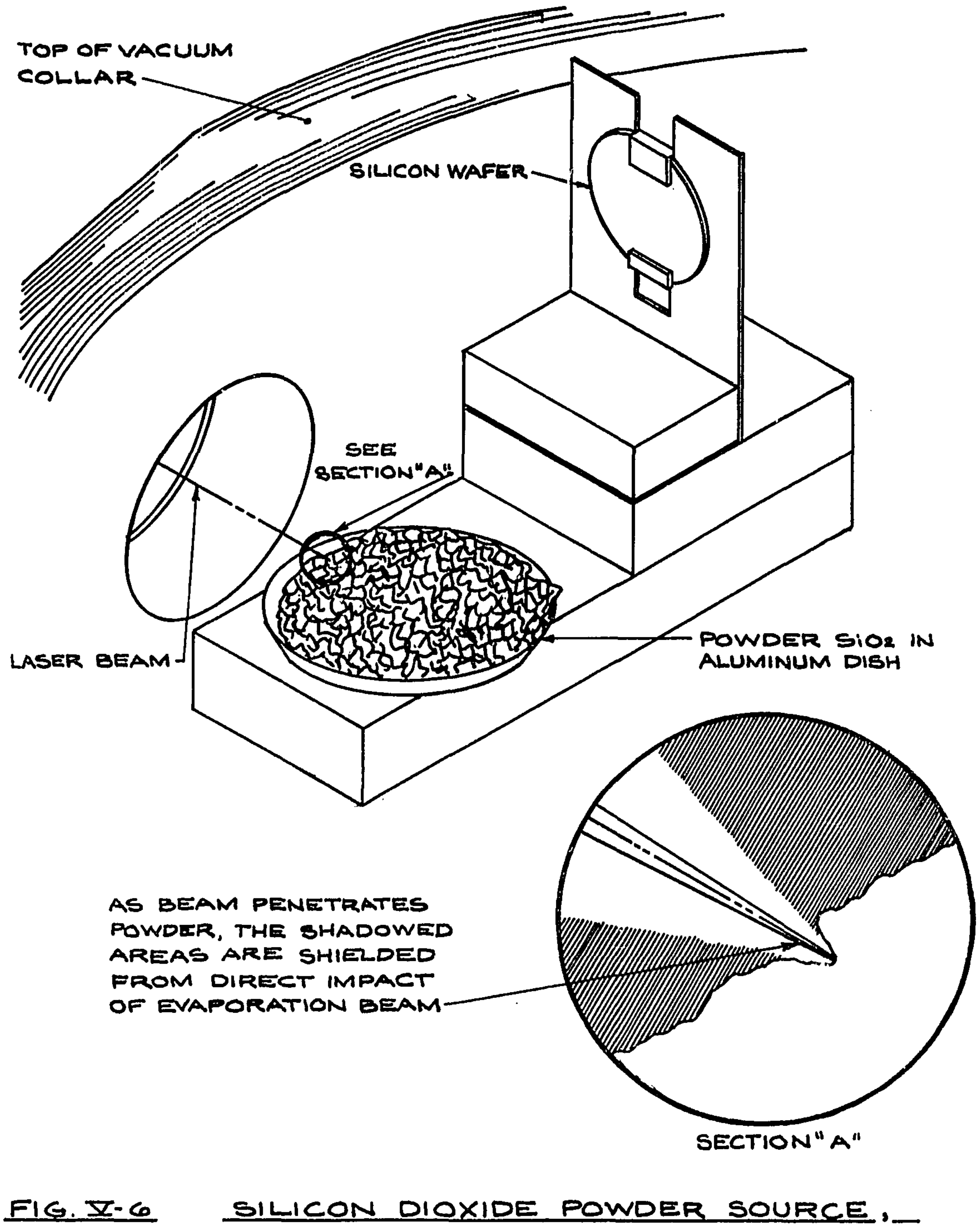

FIG. V-6 SILICON DIOXIDE POWDER SOURCE, SHOWING INDENTATION DURING EXPOSURE TO INFRA RED LASER.

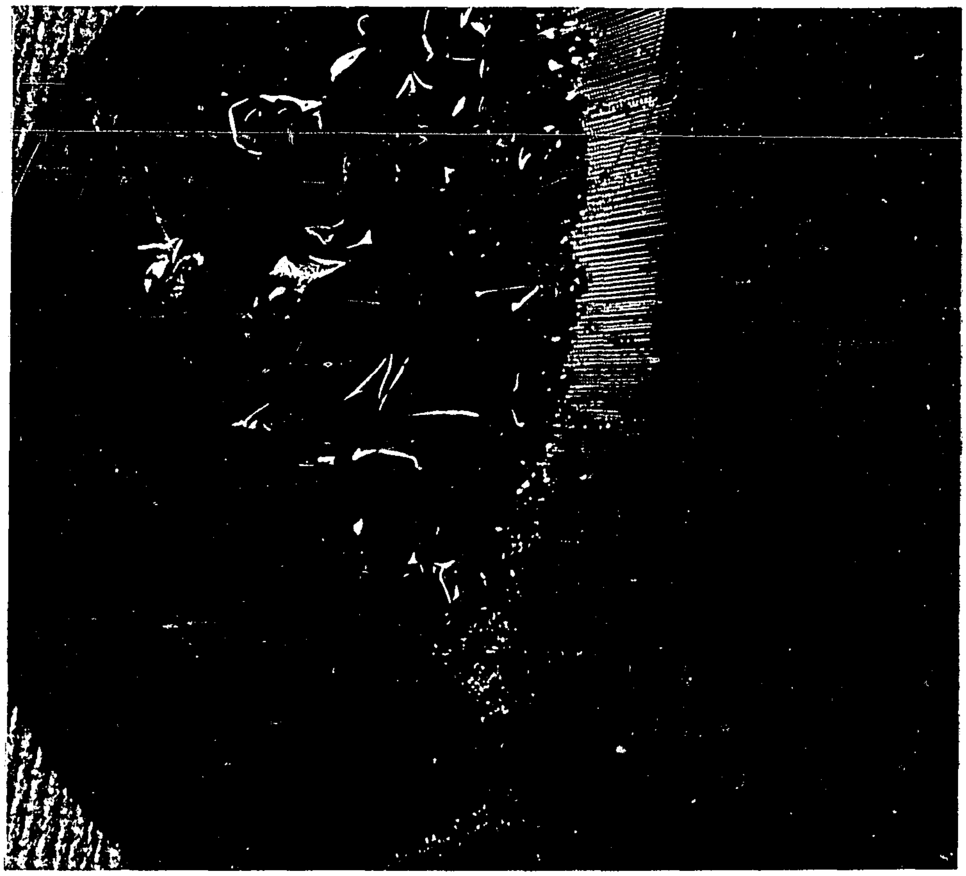

Figure V-7. Photograph of Silicon Wafer Coated With SiO_2 Evaporated Utilizing a CO_2 Laser. The highlighted film is non-adherent. The spokes separating this region from a thinner adherent film are clearly visible. The region in the lower left of this figure was covered by aluminum foil during evaporation.

strong suggestion of a diffraction pattern. A speculative explanation is that the sudden heating of the silicon dioxide powder by the concentrated CO_2 laser beam raises the temperature to the evaporating point so suddenly that a fair proportion of the molecules leave with an energy (hence momentum) within a narrow band. The diffraction might then be accounted for by the edge effect which occurs at the source (Figure V-6).

A second experiment, run with a quartz rod in place of the silicon dioxide powder, showed only slight evidence of diffraction through a double slit in the path of the silicon dioxide.

Prior experiments with evaporation by CO_2 laser were conducted by Hass and Ramsey[3] with their primary interest on coatings for optical devices. Their published results were received at Newark College of Engineering on September of 1969, after the initial experiments had been completed by this investigator.

4. Thermal Diffusion.

If the silicon wafer is cooled by a heat sink, a moderate beam of infra-red will heat a silicon dioxide coated surface without evaporating a significant quantity of silica. The equilibrium state will involve addition of energy by the laser

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[3] Hass, G. and J.B. Ramsey, "Vacuum Deposition of Dielectric and Semiconductor Films by a CO_2 Laser." Applied Optics, Vol. 8, No. 6, June 1969, pp 1115-1118.

beam in an amount which decreases with depth into the layer. Heat will be lost due to conduction to the silicon, and by convection and radiation at the surface. In a vacuum the convection will be eliminated. A thermal gradient will be established which will decrease from the oxide surface inward. This will hold until a temperature is reached at which radiation is a major mode of heat transfer.

As has been noted in Chapter II, in such a situation of temperature gradient, impurities will diffuse in such a manner that lighter molecules will move towards the higher temperature region. In terms of influencing device reliability, this may permit the inducement of certain impurities to the surface where they may then be removed with a very light etch, leaving the remainder of the thin film insulation in a much purer state.

5. Summation and Projection

Device reliability can be improved by high rate laser evaporation of films, and by film removal which does not involve chemical etch baths. Experiments have proven the capability of accomplishing the evaporation, and calculations assure the removal capability.

Short-term evaporation by 10.5 micron laser beam may also prove useful for silicon nitride depositions. Other laser frequencies may open other doors. For example, higher frequencies could be used to heat the silicon locally, raising the possibility of maskless diffusion, with a subsequent lowering of the number of processing steps and increasing reliability.

REFERENCES

[1] Hodgman, Charles D., Handbook of Chemistry and Physics, 40th Edition. Cleveland, Ohio: Chemical Rubber Publishing Company, 1959.

[2] Sohn, Kenneth, Private Communication, Newark College of Engineering, September, 1969.

[3] Hass, G. and J.B. Ramsey, "Vacuum Deposition of Dielectric and Semiconductor Films by a CO_2 Laser." Applied Optics, Vol. 8, No. 6, June, 1969, pp 1115-1118.

CHAPTER VI

CONCLUSIONS

Surface leakage in reverse biased, oxide passivated, epoxy encapsulated silicon diodes has been found to increase by a factor of 3800 during prolonged exposure to an environment of 65°C and 95 percent relative humidity. This investigator has identified the predominant mechanism to be leakage through the passivating layer in a direction normal to the surface, thence along the epoxy-silicon dioxide interface over the depletion region, then back through the oxide passivation to the conducting silicon.

Leakage within the silicon dioxide parallel to the surface was calculated with the aid of tables of comparative values to be negligible. Leakage through the epoxy was calculated on the basis of resistivity measurements of the actual epoxy to be small compared to the above factor.

The average leakage measurements on glass encapsulated, nitride passivated diodes under the same accelerated environment as the epoxy, oxide passivated diodes, showed a leakage increase by a factor of only 1.7 after 4500 hours. It was noted that control diodes (not in temperature-humidity) also increased by this very small factor of 1.7.

The very large difference in the ratio of the 0 hour to 5000 hour leakage of the two types of protective surfaces is attributed to moisture absorbtion in the epoxy resin.

As part of this dissertation, a table has been constructed containing physical properties of silicon, silicon dioxide, silicon nitride, silicon monoxide, and aluminum oxide. This table, in addition to being used to assist in determining the predominant leakage mechanism was instrumental in leading to theoretical and experimental research conclusions involving infra-red absorbtion of the insulating layer. Using a CO_2 Laser as an infra-red source:

1. Aluminum oxide and silicon dioxide films have been evaporated on silicon substrates by this technique.

2. Such film evaporations are capable of depositing high purity films more simply than can be obtained from other techniques. Such high purity enhances reliability of the device being formed.

3. Insulative films can be removed from a local spot on a silicon chip, with very little disturbance of the silicon substrate. Elimination of etching compounds is a definite reliability improvement.

4. It is speculated that silicon nitride can be deposited by this technique. Silicon nitride normally decomposes at very high temperatures.

5. Additional possibilities for reliability and device improvement using variations of this technique are discussed in this dissertation.

It was concluded that considerable information of the compatability of silicon, insulation and device use could be extrapolated from considerations of the tabulated physical parameter values. Examples are contained within involving mechanical and electrical stress, capacitive coupling, and diffusivity of ions. A further conclusion is that structure with large crystallites is to be avoided if ultra reliable devices are to be produced.

APPENDIX I

IMPLEMENTATION - EQUIPMENT AND TECHNIQUES

APPENDIX I

IMPLEMENTATION - EQUIPMENT AND TECHNIQUES

1. Introduction

In every physical research project, a certain number of fixtures and measuring devices must be constructed. This project differs in that a large number of undergraduate students participated in the development of equipment and measuring techniques. It is the purpose of this appendix to describe the extent of this participation and the equipment and techniques involved. A summary of projects and the students involved is included at the end of this appendix.

2. CO_2 Laser

The infra-red absorbing properties of silicon and protective coatings for a wavelength of 10.5 microns have been listed in Chapter III and discussed in further detail in Chapter V. At, or near this frequency, the protective coatings are very absorbent, while the silicon is virtually transparent. At higher frequencies, both become transparent, until the visible spectra is reached, at which the silicon absorbs light, with the oxides transparent. The particular usefulness of high power density at 10.5 microns has been discussed. It might be possible to generate high power densities and at this frequency by an arc or other power source, but practically speaking such sources as envisioned cannot compete with the CO_2 laser. The beam from an arc source cannot be concentrated to an area smaller than the cross section of the arc whereas the laser beam can be focused to a fine point. Further, an arc source produces a broad spectrum of frequencies, most of which would have to be discarded by reflection or absorption. To provide the end use power density required, an excessive power input would be necessary.

The CO_2 laser constructed is illustrated in Figure A-1. The two meters length of glow discharge provides a capability for power of approximately 150 watts. Crude measurements to date indicate a radiant power output of approximately 80 watts. The gas manifold on the back provides for mixture and adjustment of proportions of CO_2, Helium and Nitrogen. The mirrors are mounted inside the vacuum system to eliminate the need for Brewster's angle exits for the beam. The mirrors are adjustable by virtue of metal bellows connecting the mirrors to the fixed portion of the vacuum system. The mirrors are physically located about one foot from the entrance of the discharge tube into the end electrodes. This provides some isolation from the expected sputtering action at the electrode. One end is grounded, the other end is near ground. A resistive network in the power supply is used to balance the discharge in the otherwise parallel glow sections.

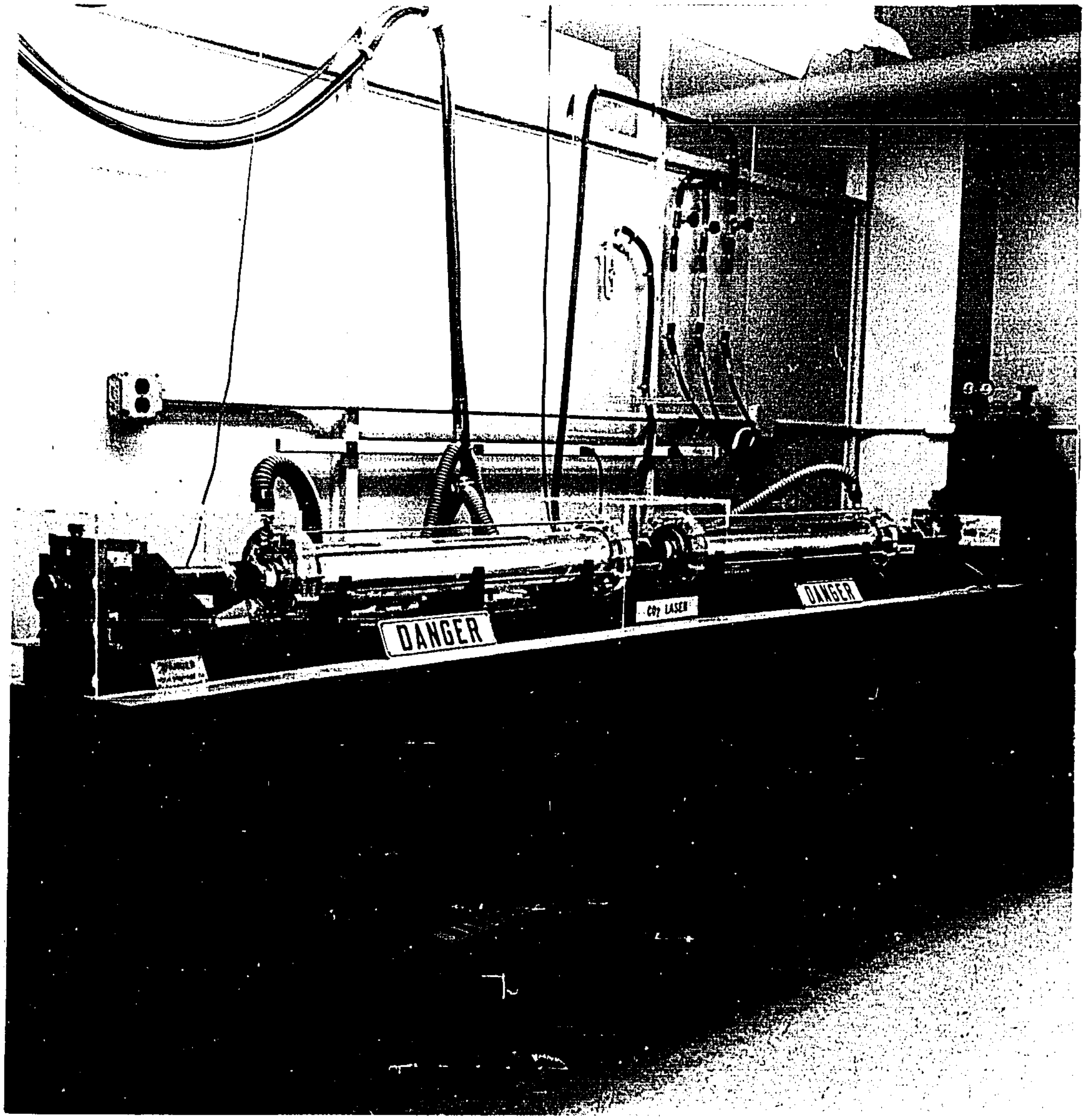


Figure A-1. CO_2 Laser Constructed for This Project.

Figure A-2 shows the concentration of the infra-red energy by means of a single crystal of potassium chloride which has been ground into a lens by the students.

3. Clean Chamber

The device for measuring dust completed as a senior project involved reflected light and a photo multiplier tube and amplifier. The principle was sound, but the unit involved a photo multiplier belonging to another laboratory and could not be permanently retained. Ultimately, a smaller unit can be constructed. The current clean chamber was purchased commercially with a matching gift from the manufacturer, providing two sections (for four glove parts). It contains an integral nylon sink and an exit directly to the quartz tube of the Hevi-Duty tubular furnace. The air is filtered into the chamber through a charcoal filter then through a Cambridge absolute filter.

The air into the room which contains the clean chamber is filtered through three elements: (a) a pre-filter, (b) a 1 1/2" thick bed of activated charcoal, and (c) a Mine Safety Appliance absolute filter. It is intended in the future to add pre-filtering by means of an electrostatic precipitator. The use of the various types of filter complement one another. The charcoal filter removes organic vapors and inorganic gases whose molecular weight differs appreciably from air. The

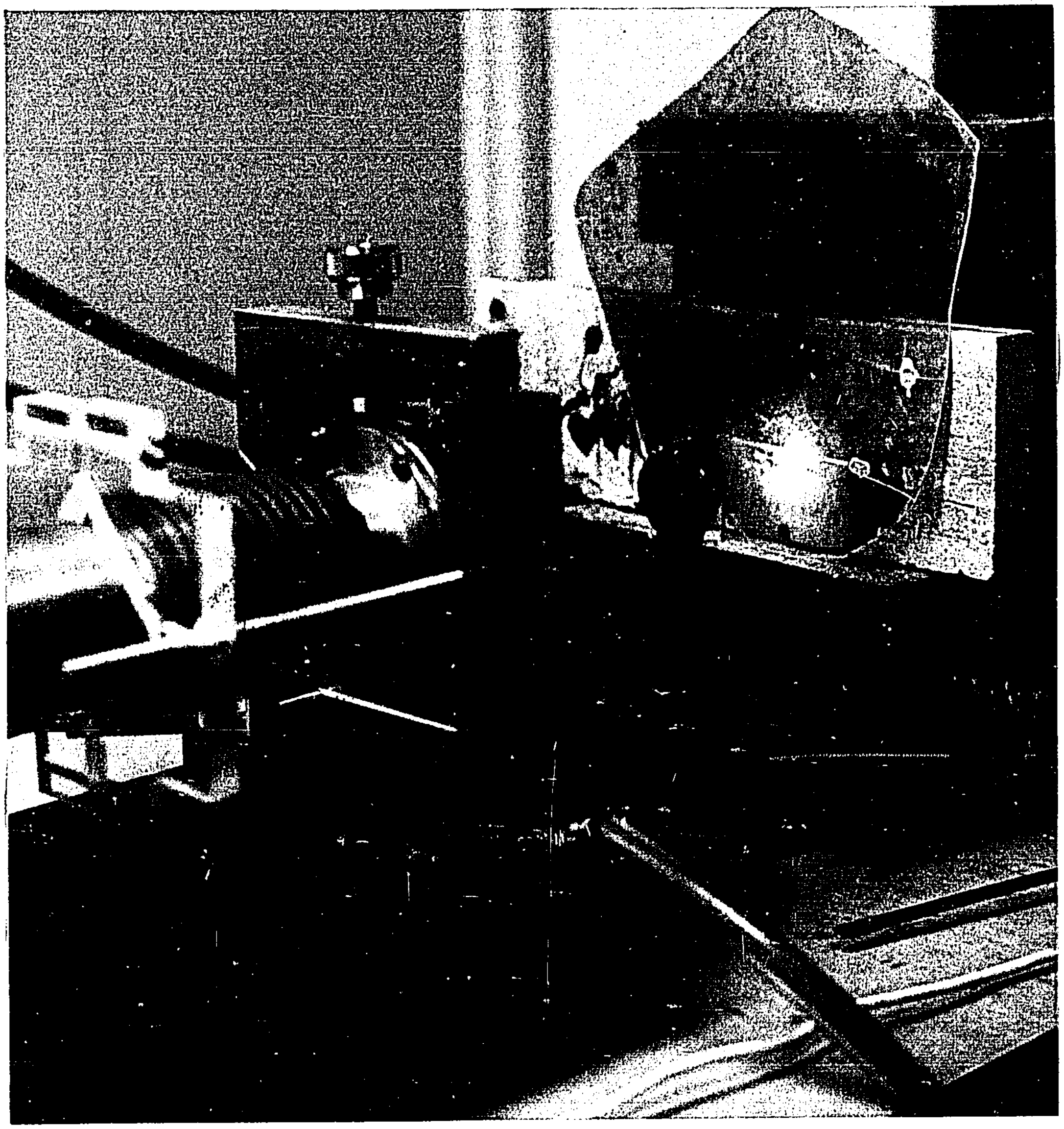


Figure A-2. Concentration of 10.5 Micron Laser Beam With a KCl Lens.

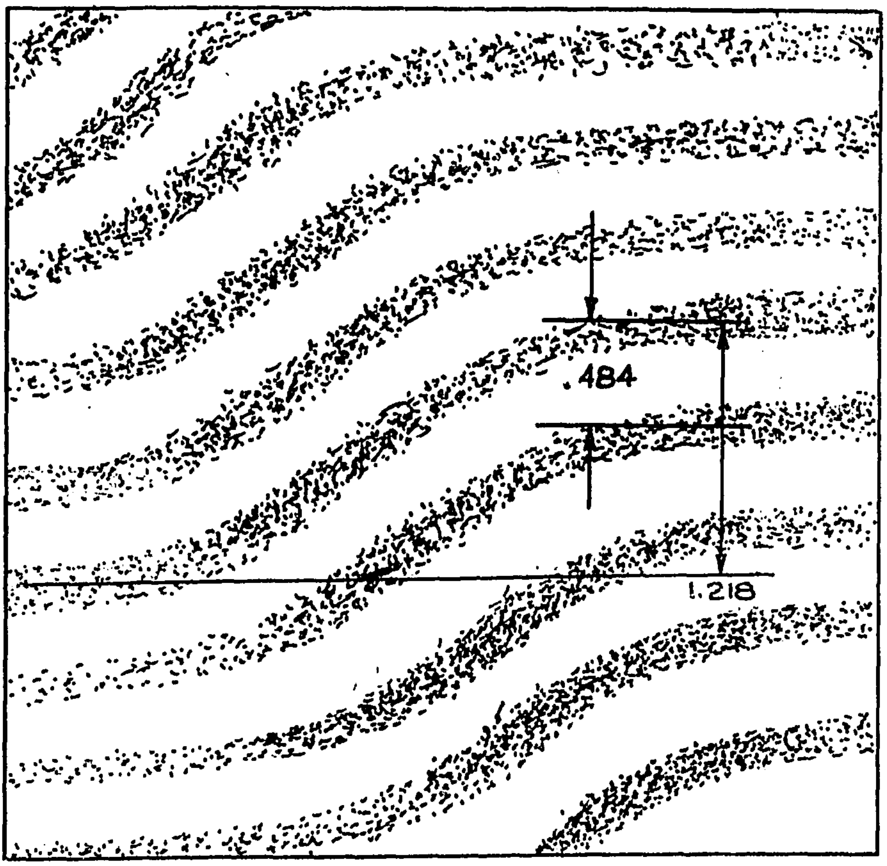
absolute filter removes 99.8% of particles above the size of .3 microns, but does very little filtering of smaller aerosols. The electrostatic filter, when added, will remove approximately 85% of all size particles, including the very small particles missed by the absolute filter.

The clean room, aside from the clean chamber, is also utilized for weighing on the Cohn Microbalance. This balance is so sensitive that a particle of dust settling on one pan could seriously alter a reading. The balance is capable of detecting a difference in weight of 0.1 micrograms, and as such is useful in weighing the very thin films involved in silicon protective layers.

4. Film Thickness, Dielectric Properties

The microbalance mentioned in the previous paragraph is suitable for measuring the weight change in formed or deposited films. In the case of grown silicon dioxide, for example, it is necessary to weigh to precision to detect only the oxygen absorbed, since the silicon is present before and after the oxidation process.

Three optical techniques were utilized in addition to the weighings. The first used a Michelson interferometer, the second a direct measurement of a step using a tilted optical flat (Fizeau's fringes), and a third method utilizing Newtons Rings. Figure A-3 is a tracing of a photograph of such



$\frac{1.218}{.484} = 2.5$ FRINGES DISPLACEMENT

$\frac{1}{2}\lambda = 2946$ Å

THICKNESS = (2946)(2.5) = 7350 Å

FIG. A-3 SKETCH OF FIZEAU'S FRINGES OF SILICON DIOXIDE GROWN ON SILICON AT N.C.E. - STEP WAS PRODUCED BY MASKING WITH WAX AND ETCHING IN HF.

fringes at a step.

Relatively simple setups were utilized for measuring dielectric strength and dielectric constant. In essence the electrodes were pools of mercury contained by "O" rings which were clamped on the oxidized silicon chip. Field strengths about one-fifth of the literature values were attained in the early films. Improvements in the air filtration system, as well as utilization of pre-polished silicon substrates and a rather elaborate cleaning cycle should result in materially improved films.

5. R.F. Sputtering Source

A radio frequency generator and an R.F. matching network for variable loads is being constructed for use in R.F. sputtering depositions and thermal decomposition depositions. A design plate power input to final stage is 1 KW and the operating frequency is 13.560 Megacycles.

6. Water Purification; Compressed Air

The exceptional reactivity of an ultra-clean silicon surface, layer thicknesses of a few thousand angstrom units, depletion widths of tens of thousands of angstrom units and the sensitivity of the final film to impurities such as sodium and factors which dictate ultra-cleanliness, particularly in water utilized in etch, rinsing and oxidation operations.

In one installation visited by this author the following steps were observed:

1. The starting water makeup was commerical deionized water piped throughout the factory.
2. The deionized water was distilled in all stainless steel container.
3. The distilled water was passed through a charcoal bed.
4. The water was then passed through an ion exchange resin bed.
5. The final water was filtered and returned to step (2) above. As used, new house deionized water would replace the unreturned final pure water.

The system in use at NCE involved the following steps:

1. Input charcoal filter
2. Commercial Cation Exchange
3. Commercial (strong) Anion Exchange
4. Bacteriological Filter, porcelain, (stainless steel case).
5. Mixed bed ion exchange unit - Polyvinyl chloride shell
6. Final Filter
7. PVC pipe and fittings to clean chamber

The NCE unit exposes no stainless steel to the ultra pure water, but at present has a serious deficiency in that recirculation is not employed. It is necessary to run the water for several minutes to achieve resistivities in excess of one or two megohm centimeters. A second disadvantage of the NCE unit is the rapid clogging of the bacteriological filter. This can only be overcome by frequent changing of this unit. Particles the size of bacteria (several microns in diameter) obviously must be removed from the system whether organic or inorganic in origin.

The distillation step <u>might</u> remove many small particles, but it should be clearly understood that the smaller the particle the more easily it might be entrained in the rapidly-moving vapor stream during distillation. This writer speculates that a useful addition to a distillation scheme would be an electrostatic precipitator in the water vapor stream.

Simon and Calmon[1] also show a sterilization lamp in the circuit, which is probably a sound addition. Filtration removes only those bacteria coming into the system and has no effect on the bacteria that grow beyond the filter. Aside from the effect of a particle this size on the final microcircuit, it is not difficult to envision a masking of ion exchange efficiency if living organisms are allowed to

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[1] Simon, G.P. and C. Calmon, "Ultrapure Water for the Semiconductor and Microcircuits Industries." <u>Solid State Technology</u>, February 1968, pp 21-30.

multiply on the resin surface.

A compressed air cleaning unit to provide ultra-clean compressed air is near completion. The compressed air can be used to blow off excess water, which can remove particulate material as well as dissolved material which might precipitate or crystallize on the substrate prior to final processing. The following units are installed:

1. Water separator
2. Commercial oil separator and filter
3. Six foot long charcoal bed
4. Six foot long molecular sieve bed

A final bacteriological filter and microporous metal filter will complete this system.

Table A-1. Undergraduate Projects Related to Reliability Research on Surfaces

Project	Students Involved	Type Project
CO_2 Laser	S. Hofra, R. Agrusti R. Snow	Senior Project
Clean Chamber - Filtration and Measurement	G. Luzniak	Senior Project
Film-Thickness Measurement	H. Orlovsky	Senior Project
Film - Dielectric Properties Measured	R. Zagier	Senior Project
R.F. Source for Sputtering (Partially Complete)	L. Skarin	Senior Project
Water Purification System	A. Simons	OEO Support

APPENDIX II

DATA

In this section the raw data applying to Chapter IV measurements are tabulated.

One notable exception is that data leading to Charts IV-1 through IV-9. This data has been previously published in Progress Reports, numbers one through twelve, for contract number DAAA-68-C-0500 between the Foundation for the Advancement of Graduate Study in Engineering (Newark College of Engineering) and Picatinny Arsenal LRPL, Dover, New Jersey.

Unless otherwise noted, all current readings were taken with a General Radio electrometer, Model 12304.

APPENDIX - II - 1

Nitride Passivated Diodes under 65°C Temperature, 95% Relative Humidity, Except for Units 1 and 2 Which Were Maintained Under Room Ambient Conditions. Six Pages of Data Follow.

(See Charts IV-11, IV-12)

Unit #1 - Nitride Passivated Diodes
45 Volts Reverse Bias - Leakage Measured in Microamps.

Diode No.	Nov. 25	Dec. 17	Jan. 8 22°C	Feb. 27 5°C	May 30 25.4°C	July 23 45V	Sept. 4 22.6°C 45V
1	.034	.040	.030	.040	.040	.038	.036
2	.008	.005	.012	.0094	.0135	1012	.011
3	.0085	.0055	.012	.094	.014	1012	.011
4	.007	.017	.022	.022	.0255	1022	.021
5	.013	.010	.0165	.015	.0195	.016	.015
6	.0076	.006	.011	.085	.014	.0115	.011
7	.012	.009	.016	.015	.0195	.016	.015
8	.011	.0075	.0155	.013	.018	.015	.015
9	.0083	.0055	.013	.0115	.015	.0125	.012
10	.0065	.0035	.010	.007	.012	.0092	.010
11	.0125	.009	.017	.012	.0205	.0165	.0165
12	.010	.0075	.0145	.013	.018	.014	.014
13	.010	.0068	.013	.0115	.016	.013	.013
14	.024	.020	.025	.026	.0275	.0235	.025
15	.15	.13	.080	.12	.090	.084	.088
16	.0055	.003	.010	.066	.012	.095	.010
17	.0125	.008	.015	.0145	.019	.015	.016
18	.0105	.007	.013	.0125	.0166	.013	.0135
19	.009	.0055	.013	.0105	.0168	.013	.013
20	.014	.0011	.018	.018	.022	.0175	.018

Unit #2 - Nitride Passivated Diodes
45 Volts Reverse Bias - Leakage Measured on Microamps.

Diode No.	Nov. 25	44 Volts Jan. 8 22°C	44-47 Volts Feb. 27 25°C	45 Volts May 30 25°C	45 Volts July 23 22.6°C	45 Volts Sept. 4 22.6°C
1	.013	.031	.016	.022	.0165	0.0165
2	.011	.015	.0145	.021	.015	.015
3	.0092	.013	.0115	.0186	.014	.0135
4	.0055	.009	.0062	.0135	.010	.010
5	.0052	.0095	.0067	.014	.0105	.010
6	.015	.016	.018	.024	.018	.018
7	.010 $\underline{\div}$ .001	.0135	.0125	.0175	.0145	.0135
8	.0073	.012	.0096	.0153	.013	.0125
9	.019	.019	.0215	.027	.022	.021
10	.0048	.0093	.0062	.0123	.0095	.0095
11	.012	.015	.015	.0213	.016	.0165
12	.015	.0195	.019	.025	.0195	.020
13	.0105	.0127	.0124	.019	.014	.014
14	.014	.017	.0176	.023	.0175	.019
15	.0055	.0102	.008	.013	.010	.0105
16	.011	.0155	.014	.0203	.015	.018
17	.0128	.0175	.0175	.023	.017	.019
18	.0096	.015	.014	.020	.015	.016
19	.0105	.015	.0145	.020	.0155	.016
20	.0084	.012	.0111	.0178	.013	.0138

Unit #3 - Nitride Passivated Diodes
45 Volts Reverse Bias - Leakage Measured on Micro-amps.
[Unit #3 Subjected to Temperature-Humidity]

Diode No.	Nov. 25	Dec. 17 21.6°	45 Volts Jan. 8 22°C	46 Volts Feb. 27 25.2°C	45 Volts May 30 25°C	45 Volts July 22 24°C	45 Volts Sept. 4 23°C
1	.0077	.0074	.012	.0107	.0125	.013	.012
2	.0064	.005	.011	.0097	.012	.012	.011
3	.0086	.0068	.013	.012	.0145	.014	.0125
4	.011	.009	.014	.013	.015	.015	.0135
5	.007	.005	.012	.0087	.0125	.0125	.011
6	.0125	.011	.0155	.015	.018	.018	.016
7	.0078	.006	.013	.010	.014	.0135	.012
8	.012	.011	.015	.015	.018	.0175	.015
9	.011	.092	.016	.015	.018	.0163	.015
10	.0068	.005	.012	.093	.013	.0127	.012
11	.014	.013	.018	.0175	.021	.0215	.018
12	.0084	.007	.0125	.010	.014	.0138	.012
13	.011	.010	.0155	.0145	.0175	.017	.018
14	.0125	.011	.0145	.0145	.018	.017	.018
15	.0155	.014	.0155	.0185	.021	.0205	.0175
16	.021	.020	.021	.025	.026	.026	.022
17	.007	.006	.012	.0091	.014	.0135	.011
18	.009	.008	.013	.0115	.016	.0165	.0125
19	.0072	.0056	.012	.0091	.0135	.0125	.011
20	.010	.0095	.0155	.015	.0185	.0165	.0145

Unit #4 - Nitride Passivated Diodes
45 Volts Reverse Bias - Leakage Measured in Microamps.
[Unit #4 Subjected to Termperature-Humidity]

Diode No.	Nov. 25	Dec. 17 21.8°C	Jan. 8 22.1°C	46 Volts Feb. 27 25.2°C	45 Volts May 30 25°C	45 Volts July 23 22°C	45 Volts Sept. 4 23°C
1	6.2 nano amp	.0053	.011	.0072	.012	.0097	.0115
2	.011 amps	.0098	.015	.0133	.0175	.0135	.015
3	.010	.0088	.014	.0125	.016	.0136	.013
4	.012	.0083	.0135	.012	.016	.013	.013
5	.0088	.0076	.013	.0105	.015	.0125	.012
6	.0125	.011	.016	.015	.019	.016	.016
7	.0075	.0064	.012	.0094	.0145	.0115	.011
8	.0105	.009	.014	.0135	.017	.014	.0135
9	.0094	.008	.013	.012	.016	.013	.013
10	.0081	.0065	.013	.011	.015	.012	.012
11	.0062	.0043	.010	.0077	.012	.010	.010
12	.0096	.008	.0135	.013	.0155	.013	.0125
13	.0065	.0052	.010	.0084	.013	.010	.010
14	.0052	.004	.0092	.0071	.0015	.0093	.0092
15	.0093	.0082	.013	.0125	.0165	.013	.013
16	.01025	.0081	.0138	.0125	.015	.0135	.013
17	.0096	.008	.012	.013	.0165	.013	.013
18	.004	.0093	.0072	.0115	.0093	.0095	
19	.025	.023	.0024	.0287	.030	.026	.026
20	.0085	.0062	.012	.0103	.014	.0115	.0115

Unit #5 - Nitride Passivated Diodes
45 Volts Reverse Bias - Leakage Measured in Microamps.
[Unit #5 Subjected to Temperature-Humidity]

Diode No.	45 Volts Nov. 25	Dec. 17 22.2°C	Jan. 8 22°C	46 Volts Feb. 27 25.3°C	45 Volts May 30 24.6°C	45 Volts July 23 22.6°C	45 Volts Sept. 4 23°C
1	.017	.016	.017	.018	.021	.018	.0185
2	.022	.021	.020	.0245	.026	.023	.022
3	.0067	.0055	.010	.0096	.0126	.011	.011
4	.011	.0095	.0138	.018	.0173	.0145	.0145
5	.0085	.0075	.012	.0115	.0145	.0122	.012
6	.009	.0084	.013	.012	.0155	.0133	.0125
7	.018	.016	.019	.020	.023	.0215	.0205
8	.011	.0105	.014	.015	.0176	.0155	.0145
9	.012	.0113	.0135	.015	.018	.015	.0147
10	.0115	.0105	.014	.014	.0175	.015	.0145
11	.0165	.015	.019	.021	.023	.0195	.0195
12	.008	.0068	.011	.0098	.0138	.0125	.0115
13	.0068	.0054	.0098	.0082	.0125	.011	.0105
14	.013	.0115	.014	.0152	.018	.016	.0152
15	.013	.0115	.0135	.015	.018	.016	.0155
16	.0095	.0082	.0012	.0123	.0155	.0133	.0132
17	.024	.021	.022	.0265	.027	.025	.0245
18	.015	.0135	.015	.018	.0206	.0175	.0175
19	.032	.036	.022	.0295	.030	.028	.0265
20	.0077	.0062	.010	.010	.0145	.012	.012

Unit #6 - Nitride Passivated Diodes
45 Volts Reverse Bias - Leakage Measured in Microamps.
[Unit #6 Subjected to Temperature-Humidity]

Diode No.	Nov. 25	Dec. 17 22.4°C	Jan. 8 22°C	46 Volts Feb. 27 25.3°C	45 Volts May 30 25.2°C	45 Volts July 23 22.4°C	45 Volts Sept. 4 23°C
1	.0105	.010	.0135	.0141	.0165	.014	.0155
2	.01025	Missing	Disconnected				
3	.009	.009	.0125	.0135	.016	.0135	.0142
4	.0086	.0074	.012	.0123	.0155	.013	.0135
5	.0175	.014	.0165	.0197	.0245	.0205	.0202
6	.009	.0065	.012	.0118	.015	.0125	.0132
7	.020	.020	.021	.022	.027	.025	.024
8	.0073	.0058	.011	.0092	.014	.012	.012
9	.035	.033	.030	Fell Out			
10	.019	.014	.0165	.0182	.023	.019	.0195
11	.007	.0055	.0105	.0085	.014	.015	.016
12	.016	.0135	.014	.015	.0195	.018	Fell out of Assembly
13	.0042	.003	.008	.0054	.0105	.0087	.009
14	.0067	.0048	.0096	.008	.0125	Fell out of Assembly	
15	.009	.007	.011	.011	.0145	.013	.0125
16	.014	.012	.0145	.016	.019	.017	.017
17	.01025	.0076	.013	.0125	.0165	.0145	.014
18	.0072	.0052	.0095	.0085	.013	.0115	.011
19							
20	.009	.0064	.0105	.0115	.0155	(?)	.0135

NOTE: Units that dropped out were still good diodes, but could not be distinguished from other loose diodes in temperature-humidity chamber.

APPENDIX - II - 2

Glass Passivated Diodes. All Units Subjected to
Tempreature Humidity After Nov. 26 Reading
All Readings in Microamps

A-II-2

Glass Passivated Diodes. All Units Subjected to Temperature Humidity After Nov. 26 Reading
All readings in microamps.

Diode No.	500 Volts Nov. 26	500 Volts Dec. 17 22°C	500 Volts Jan. 8 22.1°C	500 Volts Feb. 27 25.4°C	500 Volts May 30 25°C	500 Volts July 22 23°C	500 Volts Sept. 4 22.5°C
67	.36	.38	.40	.425	.4	.37	.32
68	.17	.20	.20	.21	.205	.166	.165
70	550	380!	broken				
71	.105	.14	.14	.13	broken		
72	.176	50	150.	100	300	100	
74	.145	.150	.150	.170	.150	.15	.115
75	.27	.30	.30	.31	.30	.27	.24
76	.32	.38	.35	.36	.33	.33	.28
77	.15	800	420	120	broken		
80	.105	250	320	260	150	100	900
81	.19	500	700	300	500	600	500
82	.185	640	550	800	200	300	226
83	.28	.35	400	.32	140	.8	.28
			Failed during reading				
84	.29	.35	.34	.382	.35	.37	.33
85	.24	420	550	640	120	170.0	120
86	.155	50	Reading went to 400, then unit broke				
87	.16	.24	.25	.22	.22	.23	.19
88	.16	350	390	410	420	330	300
89	660	600	560	520	Broken During Reading		
90	.12	.17	.16	.14	.12	.115	.09
91	.11	.14	.17	.15	.14	.15	.11
92	.09	.18	.19	.135	.18	.21	.11

APPENDIX - II - 3

Current *vs.* Voltage Curves for Nitride Passivated Diodes Under Reverse Bias.

A - II - 3

Current *vs*. Voltage Curves for Nitride Passivated Diodes Under Reverse Bias

Diode #1

0 μ amps	at	0 Volts
0.0045	at	13 Volts
0.0065	at	24 Volts
0.009	at	32 Volts
0.014	at	45 Volts

Diode #2

.019 μ amps	at	45 Volts
.013.5	at	36 Volts
.008.5	at	24 Volts
.006.5	at	16 Volts
.003.5	at	6 Volts
0	at	0 Volts

See Figure IV-10, p 167

APPENDIX - II - 4

Nitride Passivated Diodes. These Diodes were Subjected to additional stresses as described in Chapter IV - (7 Pages Following). (See text, pp 162-165)

Time (Hours)	Date
0	May 25 (1969)
240	June 4
744	June 29
1320	July 23
2376	Sept. 5

Unit #1*. A second set of Si_3N_4 passivated diodes. This particular unit was subjected to a 400 volt stress radially inward toward the lead axis. Aged at 60°C, with no deliberate humidity condition.

Diode No.	May 25 T = 24.8°C	June 4 25°C i (microamps.)	June 29 22°C Room Temperature i (microamps.)	July 23 45 Volts	Sept. 5 22.4°C 45 Volts (RCA Meter)
1	13.8	.0165	.014	.0155	.015
2	8.7	.0110	.009	.0107	.0103
3	14.5	.0174	.015	.016	.016
4	17.6	.020	.0175	.019	.0183
5	9.9	.0124	.0105	.0115	.011
6	9.3	.0115	.0095	.0106	.010
7	14.7	.0165	.0135	.0152	.015
8	16.	.0175	.015	.0163	.016
9	14.0	.0155	.013	.0145	.014
10	12.0	.0132	.011	.0125	.012
11	16.5	.0171	.014	.0156	.0155
12	14.5	.0145	.012	.0138	.0135
13	15.5	.0155	.013	.0145	.014
14	17.0	.0170	.014	.0155	.015
15	14.5	.0145	.012	.0133	.013
16	14.3	.0148	.0125	.014	.0138
17	12.0	.0134	.010	.0112	.011
18	14.5	.0139	.011	.0122	.012
19	24.0	.0240	.0195	.021	.021
20	16.5	.0165	.013	.0145	.0142
21	17.0	.0195	.015	.016	.016
22	19.5	.0205	.016	.017	.018

Unit #2*. Control Unit

Diode No.	May 25 T = 25.2°C 45 Volts i (μ amp.)	July 23 T = 23 45 Volts i (μ amp.)	Sept. 5 T = 22.2°C 45 Volts RCA Micro-Ammeter
1	.009	.0092	.013
2	.0088 (after bend)	.0087	.0135
3	.0072	.0074	.011
4	.0165	.015	.020
5	.0068	.0072	.010
6	.0095	.0092	.0122
7	.080	.080	.090
8	.010	.010	.014
9	.014	.013	.017
10	.008	.0078	.0118
11	.0056	.0054	.0091
12	.0175	.019	.020
13	.026	.0235	.028
14	.013	.013	.0162
15	.0157	.015	.023
16	.0069	.0065	.012
17	.003	.0038	.0084
18	.021	.019	.0255
19	.009	.009	.015
20	.010	.0084	.0159
21	.012	.0105	.0165
22	.0105		

Unit #3. Silicon Nitride Passivated Diodes, Subjected to a temperature of 65°C, relative humidity approximately 90% and a pulsating reverse voltage of 45 Volts.

Diode No.	May 25 T = 25.1°C i (μ amps.)	Sept. 5 22.2°C 45 Volts RCA Micro-Ammeter
1	.010	.0196
2	.011	Between .090 - .100
3	.0152	.0272
4	.017	.0216
5	.0155	.0295
6	.0145	.028
7	.0095	.016
8	.007	.0164
9	.0105	.037
10	.0063	.0185
11	.0125	.0172
12	.0094	.018
13	.0105	.0242
14	.010	.018
15	.0102	.025
16	.0132	.025
17	.011	.0161
18	.013	.0292
19	.0115	.025
20	.0105	.026
21	.0115	.021
22	.018	.028

Unit #4*. Silicon Nitrate Passivated Diodes, Subjected to a temperature of 65°C, relative humidity approximately 90% and a pulsating reverse voltage of 45 volts.

Diode No.	May 25 T = 26.3°C i (μ amps.)	Sept. 5 T = 22.5°C 45 Volts RCA Micro-Ammeter
1	.017	.031
2	.018	.035
3	.007	.019
4	.0095	.026
5	.013	.021
6	.0165	.0242
7	.0185	.036
8	.016	.033
9	.0135	.026
10	.0215	.0462
11	.0102	.022
12	.0153	.024
13	.0195	.038
14	.013	.025
15	.0265	.023
16	.0137	.020
17	.029	.035
18	.018	.034
19	.0092	.019
20	.0135	.036
21	.007	.014
22	.007	.014

Unit #5*. Silicon Nitride Passivated Diodes, Subjected to a temperature of 65°C, relative humidity approximately 90% and a pulsating reverse voltage of 45 volts.

Diode No.	May 25 T = 24° C	Sept. 5 T = 22.2°C 45 Volts
1	.0078	.020
2	.007	.021
3	.0058	.0202
4	.0078	.022
5	.0105	.029
6	.021	.033
7*	.0105	.019
8	.016	.022
9	.083	.016
10	.012	.024
11	.026	.029
12	.030	.016
13	.0105	.019
14*	.020	.028
15*	.013	.0262
16*	.0115	.024
17	.0115	.0273
18	.0125	.020
19	.011	.024
20	.015	.022
21	.035	.056
22	.015	.028

*Note: On Saturday, May 24, it was noted that the coatings on several diodes of this unit were wrinkled, exposing the glass underneath.

Unit #6*. Silicon Nitride Passivated Diodes. This particular unit was subjected to a 400 volt stress radially inward toward the lead axis. Aged at 60°C, with no deliberate humidity condition.

Diode No.	May 25 26°C i (μ amps.)	Measurement after wrapping with tin foil to provide field 25°C i (μ amps.)	July 23	Sept. 5 22.5°C 45 Volts
1	.0125	.0155	.0158	.015
2	.0094	.013	.0135	.0125
3	.0105	.0141	.0145	.014
4	.0084	.0138	.013	.013
5	.008	.0119	.0123	.0125
6	.0115	.015	.015	.0157
7	.011	.0148	.015	.0143
8	.0115	.0150	.015	.015
9	.009	.0130	.0132	.013
10	.0105	.0145	.015	.014
11	.012	.0155	.016	.0157
12	.0215	.0255	.0238	.024
13	.0115	.0149	.0145	.0144
14	.029	.030	.029	.0295
15	.0115	.0150	.0155	.015
16	.0138	.0174	.017	.017
17	.017	.0200	.0195	.020
18	.0145	.0180	.0178	.0178
19	.0135	.0155	.0158	.0155
20	.0102	.0140	.0135	.0137
21	.008	.012	.0116	.0115
22	.0115	.0145	.014	.014

Unit #7*. Silicon Nitride Passivated Diodes. Control Unit.

Diode No.	May 25 T = 27°C μ amps.	July 23 T = 22.8°C 45 Volts μ amps.	Sept. 5 T = 22.8°C 45 Volts μ amps.	Sept. 5 Duplicate Set of Readings. However taken with RCA Micro-Ammeter
1	.013	.010	.014	.015
2	.0068	.0064	.010	.011
3	.0095	.0085	.0125	.0135
4	.0115	.010	.01425	.015
5	.0145	.0125	.0175	.018
6	.0105	.0095	.0142	.014
7	.023	.0205	.0265	.025
8	.011	.0125	.0135	.0142
9	.0125	.0135	.0155	.0158
10	.0084	.0105	.0122	.0123
11	.0087	.011	.0121	.0123
12	.011	.012	.0133	.014
13	.0064	.0084	.010	.012
14	.0102	.0122	.013	.0142
15	.0105	.0122	.0133	.015
16	.0185	.0195	.020	.021
17	.0115	.0115	.0138	.015
18	.0066	.0096	.0102	.012
19	.0125	.014	.0145	.016
20	.0088	.0115	.012	.0135

APPENDIX - II - 5

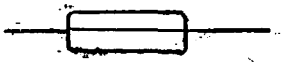
Visual Inspection Report
Glass Passivated Diodes

A - II - 5

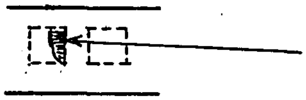
Visual Inspection Report
Glass Passivated Diodes

#69 Pulled on leads, unit separated into two pieces.

#89 Very straight crack (along axis) in glass!



#92 Glass apparently not completely bonded to metal electrodes or studs.



Half-moon section appears milky

#84 Bond looks very smooth in area of junction, but one glass end termination is rough.

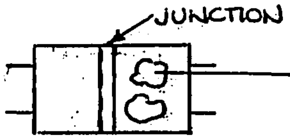
#77 Surface of glass chipped near numbered end

#88 Glass off center

Also extra piece of glass about here

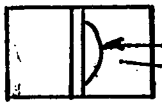
#85 O.K.

#91



Glass surface indented and black. Deposits on indentation.

#87



Half-moon section clear.
This part appears milky.

#80 Looks good -- very slightly off center.

#73 Cracked Glass -- also red fleck of material on surface of glass.

#74 O.K. But surface of glass is rough on spots.

#72 O.K. But electrode nearest number is diffuse, the other polished.

#76 Glass appears to contain a bubble.

#67 O.K.

#71 Glass rough. Appears to have one large multi-shaped bubble running along junction

#68 Rough glass

#78 Cracked Glass.

#70 Cracked Glass.

#81 O.K.

#90 Large bubble on glass. Rough glass crevasse reached into junction thru glass.

#86 O.K. Two rough spots.

#82 Glass off center and rough, but seal looks good.

#75 O.K.

APPENDIX - II - 6

Leakage Current, Epoxy Headers

APPENDIX - II - 6

LEAKAGE CURRENT, EPOXY HEADERS

Leakage current nanoamperes, in 25 epoxy headers, remaining after active SCR elements had been removed by filing. [See Figure IV-6].

Time shown is after exposure to 65°C, 95% Relative Humidity.

0 Hours

0.01	0.01	0.25	0.20	0.08	0.01	0.20	0.08	0.02	0.16
0.20	0.09	0.01	0.01	0.20	0.14	0.01	0.25	0.01	0.01
0.20	0.01	0.01	0.04	0.25					

1000 Hours

0.20	1.50	1.00	1.30	0.20	1.10	0.20	1.10	0.20	1.40
1.50	0.01	4.00	0.20	2.00	1.00	1.00	1.50	1.60	0.10
1.90	0.90	0.01	2.00	1.10					

2000 Hours

0.10	1.20	1.00	0.10	1.20	0.30	1.30	0.50	0.30	1.30
0.50	1.60	0.50	1.20	1.20	0.10	0.01	1.80	0.60	1.30
0.70	0.01	1.40	0.50	0.90					

3000 Hours

0.10	1.40	0.10	2.10	0.90	0.01	0.20	1.40	1.60	0.01
0.01	1.70	0.05	2.00	0.03	2.70	0.04	1.70	2.60	0.01
2.00	0.20	0.60	0.10	0.90					

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